11

# Illustrated World of Science Encyclopedia

Chemistry II:
INORGANIC AND
ANALYSIS

# THE WORLD OF SCIENCE

**STEEL INGOT DURING WEIGHING**—The oxidized layer on the surface of the incandescent mass tends to break away from the steel ingot.

# THE WORLD OF SCIENCE

VOLUME

11

## CHEMISTRY II

## Inorganic Chemistry and Analysis

*with*

The Illustrated Science Dictionary

**CREATIVE WORLD PUBLICATIONS, INC.**
CHICAGO

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## VOLUME 11

# CHEMISTRY II

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# CHEMISTRY II

## Concepts of Chemistry

### INTRODUCTION

Chemistry is more than a study of elements and their properties. More properly, it is a science devoted to examining the vast number of interactions among chemical species. In fact, the scope of chemistry has become so extensive that it has been divided into several subdisciplines.

The traditional chemistry practiced for several centuries approaches most closely the modern field of inorganic chemistry. This field is responsible for studying interactions among the elements. Because of the length of time inorganic chemistry has been studied, the interests of scientists in this field today bear little resemblance to those of the past. Contemporary inorganic chemists are concerned with the interesting structures of boron and phosphorus compounds, primarily because of boron's unusual ability to bond to itself, and because of the importance of phosphorus compounds to modern society. Also currently important is the catalysis of chemical and physical reactions by the noble metals and transition metals.

Carbon, like boron, is capable of bonding to itself and other elements, thereby forming a large number of compounds. For this reason and because of the importance of carbon compounds in living systems, a separate branch of chemistry—organic chemistry—has developed just for the study of these compounds. This active field is responsible for the development of many important chemical products, from plastics to drugs. Reflecting this importance, Volume 12 of this series has been entirely devoted to organic chemistry.

The complexity of chemical interactions and the sophisticated tools necessary for their study have given rise to another branch of chemistry—physical chemistry. This field draws heavily on recent advances in physics and the science of measurements to characterize, examine, and analyze chemical systems theoretically. Physical chemistry is responsible for many advances in other fields of chemistry, since these fields often rely on its concepts to predict the behavior of chemical entities.

Because it is necessary to test for purity of inorganic and organic substances and to analyze mixtures of them, the field of analytical chemistry was formed. This branch of chemistry traditionally served a subsidiary function and was used to determine the chemical composition of a sample by means of various chemical tests. Although older analytical methods are still employed, modern analytical chemistry encompasses a far greater area and has, indeed, become the science of measurement of chemical systems. Physical testing methods such as spectroscopy, electrochemistry, and even nuclear reactions are now used by the analytical chemist.

Although the divisions of chemistry have arisen as described, it is becoming increasingly recognized that each branch depends extensively on the other branches and other sciences. For example, the importance of chemistry to biological systems has caused the field of biochemistry to become recognized as perhaps the most significant area of chemical research. Also, the necessity for industrial implementation of chemical processes has accelerated the development of chemical engineering.

This volume treats the concepts of chemistry on which all the fields of chemistry must draw, from the most basic distinctions between mixtures and chemical compounds to various aspects of nuclear chemistry. Types of reactions, the nature of chemical reactions, and the ways in which atoms combine are discussed. Physical characteristics of chemical systems are also examined, and simple techniques of chemical analysis are introduced. From these, the most basic concepts of chemistry, have come the advances in knowledge responsible for much of today's technological progress.

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# MIXTURES AND CHEMICAL COMBINATIONS

## marriage and divorce in chemistry

1

**HOW TO PREPARE A MIXTURE**—Powdered sulfur is mixed with iron filings to form a mixture whose components can easily be separated by mechanical means.

**MIXTURE OF SULFUR AND IRON**—Some iron filings and sulfur are placed in a mortar (the ratio should be 3:5 by weight) and blended together with a pestle until the mixture turns a grayish color and the particles of iron and sulfur are indistinguishable from each other.

2

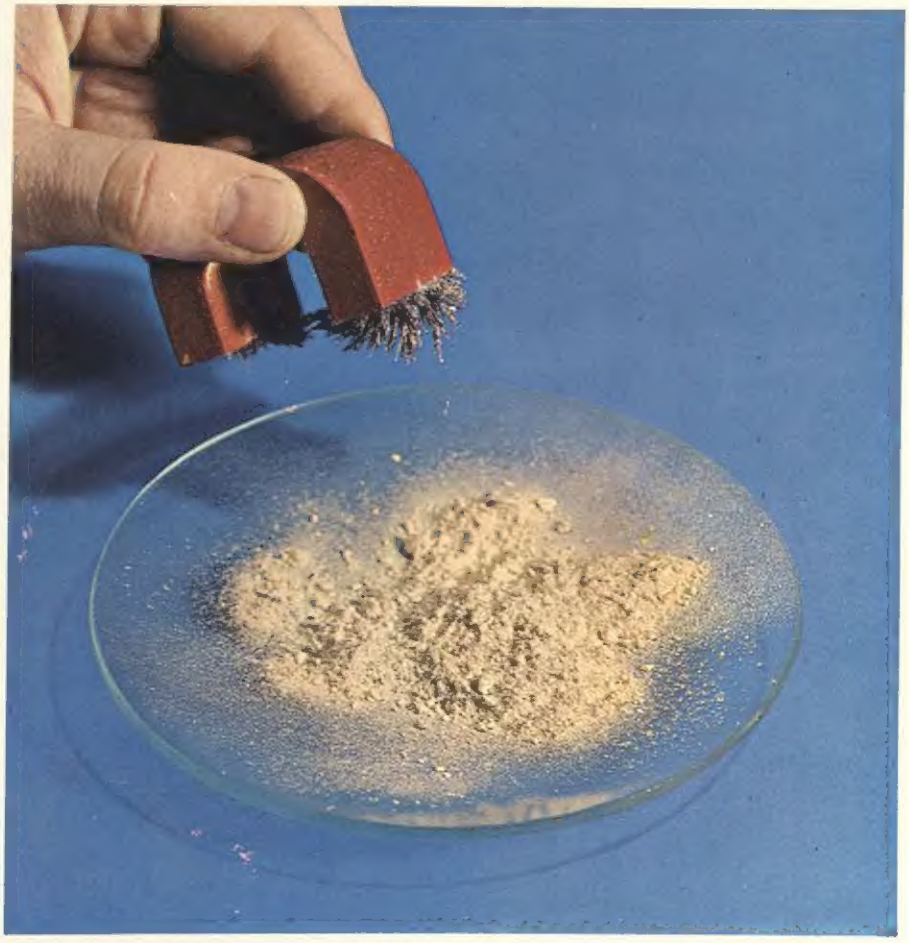
This article describes how to prepare iron(II) sulfide and hydrogen sulfide. Before going into details, however, it is necessary to mention a concept that is of great importance in chemistry—the difference between a mixture and a compound. A mixture is an intimate blend of particles (which may be submicroscopic) of different substances. Even though the particles are perfectly blended, they do not react with each other and they can be separated by mechanical methods. An example of a mixture is powdered sulfur and iron filings stirred together; the iron is easily separated from the sulfur by a magnet.

In preparing iron(II) sulfide and hydrogen sulfide, the materials needed are: 30 to 50 g of powdered sulfur; 50 g of fine iron filings; 50 g of hydrochloric acid; several test tubes; 1 beaker (any size); 1 Bunsen burner; 1 mortar and pestle; and 1 magnet.

The mixture is prepared by first weighing out a little more than 3 g of sulfur and a little more than 5 g of iron filings on scales accurate to the gram. Without scales, it is possible to weigh out a quantity of iron and a quantity of sulfur so that the weight ratio is 3:5 (the volumes are approximately the same). The iron and sulfur are placed in the mortar and blended together with the pestle until the mixture turns a grayish color and the particles of iron are indistinguishable from the particles of sulfur. This is the

**SEPARATING THE MIXTURE**—A magnet separates the components of the mixture, proving that the two substances have blended physically, not chemically.

3



4a

4b

**COMBINATION BETWEEN IRON AND SULFUR**—A wooden clothespin or clamp is used to hold a test tube containing a little of the iron-sulfur mixture over a Bunsen burner flame (Illustration 4a). When the mixture is heated slowly and carefully, the sulfur melts, swells, and reacts to form a dark mass with the iron (Illustration 4b).

**IRON(II) SULFIDE**—When the test tube containing the red-hot iron-sulfur mass is plunged into cold water (Illustration 5), the glass will break and brown and metallic-looking grains will drop to the bottom of the beaker. These grains are the chemical compound iron(II) sulfide.

mixture; the iron and sulfur are not chemically bound together—they can be separated simply by dipping a magnet into the mixture. This is proof that the two elements are mixed and not chemically combined.

The chemical combination—the reaction between iron and sulfur— is initiated by placing 2 or 3 g of the mixture in a test tube and holding it over a slightly inclined lighted Bunsen burner. As the mixture is heated (this should be done slowly and carefully), sulfur dioxide vapors are usually produced. (Windows should be kept open to avoid the danger of inhaling the sulfur dioxide vapors.) The sulfur melts and swells as the heat increases. It finally glows brightly and forms a brownish, almost black, mass with the iron as reaction takes places. The test tube is then removed from the flame after five or six minutes. The mixture will be red-hot. When the tube is plunged into a beaker half full of water, the glass will shatter on contact with the water and grains of a brownish, metallic-looking substance will drop out. This is the chemical compound iron(II) sulfide, prepared according to the reaction:

$$Fe + S \rightarrow FeS.$$

5

6a

**HYDROGEN SULFIDE** — If hydrochloric acid is added to a few grains of iron(II) sulfide, a gas with an unpleasant odor is produced. This gas is hydrogen sulfide. Its acid properties are shown by a universal indicator (normally yellow), which turns pale red (Illustration 6a). Lead acetate paper, which turns brown (Illustration 6b), identifies the gas as hydrogen sulfide. If Ac refers to the acetate radical, the reaction is:

$$Pb(Ac)_2 + H_2S \rightarrow PbS\downarrow + 2HAc.$$

6b

This compound is stable; the iron and sulfur can no longer be separated by physical means. The new compound no longer has magnetic properties; it is unaffected by the magnetic field of the magnet. Any unreacted iron filings, however, will be affected by the magnet.

In the preparation of hydrogen sulfide, the grains of iron(II) sulfide are removed from the beaker, placed in a test tube, and covered with water. Two drops of hydrochloric acid are added and the tube is shaken. Reaction with HCl causes small bubbles of gas to escape from the pieces of iron(II) sulfide. This gas—hydrogen sulfide—has an unpleasant odor, much like rotten eggs. The reaction is:

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S.$$

7

The last preparation is best done in the open air, in a well-ventilated room, or under a hood. Hydrogen sulfide is poisonous, and its smell is quite intolerable to some people. To stop the reaction between the acid and the iron(II) sulfide, the sulfide is simply washed in large amounts of water.

Hydrogen sulfide can also be formed by destructive distillation of coal and by heating sulfur with hydrocarbons such as paraffin, petroleum oil, and methane.

---

**HYDROCHLORIC ACID** — If sulfuric acid ($H_2SO_4$) is added gradually to a beaker containing common salt (NaCl), hydrochloric acid is produced. This substance causes a universal indicator (normally yellow) and litmus paper (normally blue) to turn bright red.

# THE KINETICS OF REACTIONS

## systems in search of equilibrium

A piece of iron left in the open will be completely rusted after a few days in humid weather or a few months in dry weather. If a flame is applied to a can of gasoline, the fuel will be consumed in a few seconds or a few minutes.

The presence of iron in the first case, and of gasoline in the second, constitutes an unstable situation. Neither iron nor gasoline is stable in the presence of oxygen. Stability comes when the iron is combined with oxygen, and when oxygen is combined with the carbon and hydrogen of gasoline. Once the combination of iron or gasoline with oxygen has started, it will continue by itself. The fact that these reactions occur, however, is distinguished from the rate at which they occur. It is the task of chemical thermodynamics to discover the state in which a mixture of substances is stable and not liable to react. It is the task of chemical kinetics to study the speed at which such reactions take place.

Although both chemical thermodynamics and chemical kinetics deal with the development of reactions, a fundamental difference exists between the two. Chemical thermodynamics can establish (by studying the physical characteristics of substances) whether or not substances will react when mixed together. The speed at which that reaction will proceed can be established by performing and timing the experiment.

Chemical kinetics is, therefore, an empirical science, although it is possible to study the conditions under which the reaction is to be carried out and to predetermine the factors likely to accelerate or slow that reaction.

### WHY CHEMICAL KINETICS IS STUDIED

In producing a substance commercially, the first step is to determine the speed at which it will be produced. For example, if the production of a substance requires the introduction of two reagents into a reaction container, it is desirable to know the best speed at which to introduce them. Similarly, if heat is a factor in the production process, it is useful to know the temperature most favorable to the reaction desired. Such information contributes to economical and efficient production.

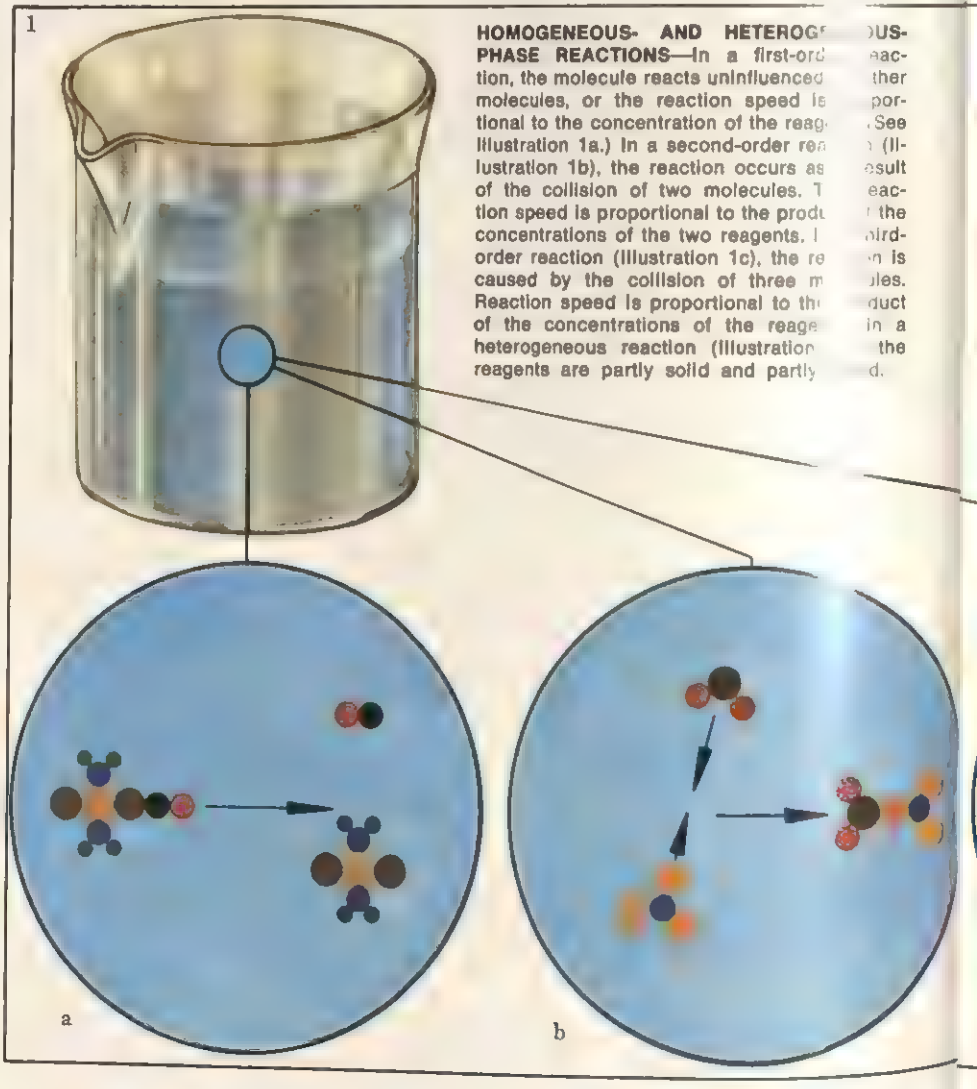
Chemical kinetics is not only the starting point in planning chemical operations, but the science that explains how reactions develop.

### CLASSIFICATION OF CHEMICAL REACTIONS

Before the speed of chemical reactions can be studied, the reactions must be classified. Homogeneous reactions are those that take place in a single phase (that is, any homogeneous part of a system that is physically distinct and separated from the others by well-defined limits). Homogeneous reactions include those that develop in a solution (in a single liquid phase) or in a mixture of gases (in a single gaseous phase). Gas mixtures are always homogeneous.

Illustrations 1a, 1b, and 1c show homogeneous-phase reactions taking place in a beaker of liquid. The liquid consists of reagents and their reaction products in solution.

Illustration 1d shows a heterogeneous-phase reaction—one that takes place in more than one phase. In the case shown, the substances are partly solid and partly liquid; these can be either the mixing




**HOMOGENEOUS- AND HETEROGENEOUS-PHASE REACTIONS**—In a first-order reaction, the molecule reacts uninfluenced by other molecules, or the reaction speed is proportional to the concentration of the reagent. See illustration 1a.) In a second-order reaction (illustration 1b), the reaction occurs as a result of the collision of two molecules. The reaction speed is proportional to the product of the concentrations of the two reagents. In a third-order reaction (illustration 1c), the reaction is caused by the collision of three molecules. Reaction speed is proportional to the product of the concentrations of the reagents in a heterogeneous reaction (illustration d) the reagents are partly solid and partly liquid.

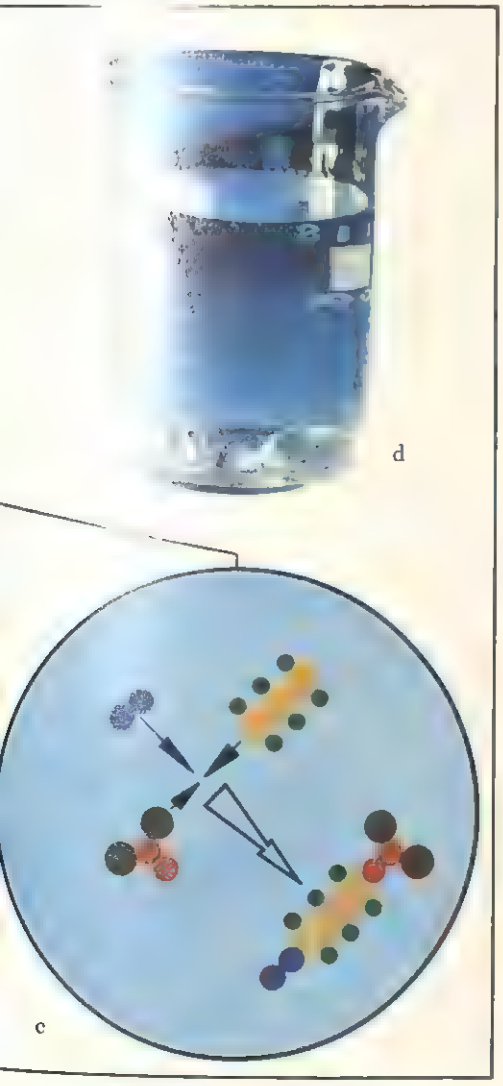
materials or the reaction products. Homogeneous-phase reactions can be divided into those that take place as a result of the transformation of isolated molecules (such as their splitting); and those that take place as a result of two or more molecules colliding.

When a molecule undergoes reaction uninfluenced by other molecules (Illustration 1a) it is called a first-order reaction.

When the reaction is caused by the collision of two molecules (Illustration 1b) it is a second-order reaction.

Third-order reactions are those in which three molecules must collide simultaneously for the reaction to take place (Illustration 1c).

A collision of four molecules simultaneously is too rare to warrant practical consideration.



d

c

2

**ENERGY OF REAGENTS AND REACTION PRODUCTS**—The sphere on the left is a conventional representation of a highly unstable molecule which is not in equilibrium. On the right, the molecule has reached equilibrium (as the uniform color symbolically shows) after splitting and liberating its excess internal energy.

In either a liquid or a gas, the molecules are in constant motion and frequently collide, although generally only two molecules are involved in each collision. Occasions in which three molecules collide are rarer, which means that third-order reactions generally proceed more slowly than first- or second-order reactions.

## FIRST-ORDER REACTIONS

Some molecules are unstable, in that they may split spontaneously—not as a result of external causes, but because of factors inherent in their structure. The energy content of such a molecule is extremely high in comparison with that of the products after it splits; the difference in energy is liberated by the splitting. Illustration 2 shows such an unstable molecule as the left (banded) sphere; the right sphere represents the same molecule after splitting and releasing its internal energy—the molecule is now in equilibrium, symbolically indicated by one color.

Before examining the law governing this process of decomposition reaction, it is interesting to note that the law is applicable not only to molecules but also to atomic nuclei that undergo the reaction known as radioactive disintegration. The nuclei of a radioactive element all disintegrate because of their internal instability rather than as the effect of external forces.

The law is as follows: The speed at which a first-order reaction proceeds depends on the concentration of substance undergoing transformation. The greater the instability of this substance, the greater the reaction speed. Furthermore, this speed is at all times proportional to the quantity of matter (that is, to the number of unstable molecules or radioactive atoms) still to undergo transformation.

## SECOND-ORDER REACTIONS

Second-order reactions occur when two molecules collide. A typical example of such a reaction is:

$$\text{hydrogen} + \text{iodine} = \text{hydrogen iodide}$$
$$H_2 + I_2 \rightarrow 2HI$$

where a molecule of hydrogen must collide with a molecule of iodine for the reaction to take place, which it does in the gaseous phase. The law governing second-order reactions states that the reaction speed is proportional to the product of the concentrations of the two reagents and inversely proportional to the concentration of the reaction product. This is clear from the fact that a collision between two different molecules, which makes the reaction possible, is the more probable the more molecules of the two types there are in a given volume. Because the reaction product is also capable of redissociating into its components, this causes the reverse dependence.

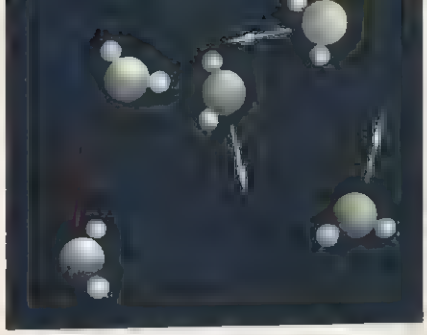
## THE EFFECT OF TEMPERATURE

In both liquids and gases it is the temperature that determines the speed at which collisions between molecules occur. The higher the temperature, the greater the speed at which the molecules in a fluid move (Illustration 3). At higher temperatures, therefore, the average number of molecule collisions is greater and the ensuing reactions normally proceed at a higher speed. Illustration 3 shows molecules of water; the large spheres are oxygen atoms and the small ones hydrogen atoms. If two molecules of water collide at high speed, they may split, as evidenced by the fact that heating water vapor to many thousands of degrees causes the molecules to collide much more frequently and to split into hydrogen and oxygen atoms.

## CRITICAL ACTIVATION ENERGY AND DIVISION OF INTERNAL ENERGY

The simplest way of explaining how a reaction such as a second-order reaction works is to attribute the cause of the reaction to a collision between the two reacting molecules. However, the collision hypothesis, although necessary, is not sufficient to justify the occurrence of the reaction. The justification needed is that a molecule should, during collision, acquire a quantity of energy exceeding a minimum value known as the critical activation energy, or the activation energy. If the molecules in collision are not activated—that is, if they do not acquire energy over and above critical energy—the collision does not provoke a reaction.

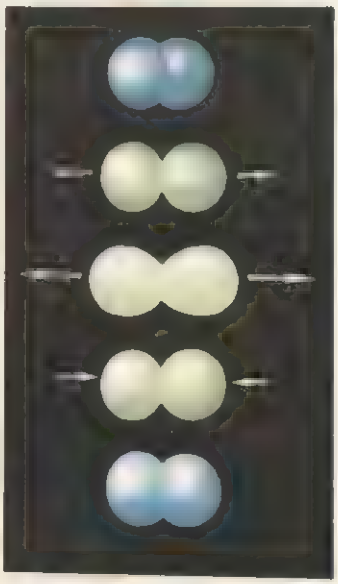
However, this activated collision theory depends on the hypothesis that molecules can be regarded as rigid spheres and that they reach the level of critical activation energy simply by increasing their kinetic energy as a result of collision. This may be true in the case of some of the simpler molecules, but it is not true in the case of slightly more complex molecules, whose internal energy consists of other forms of energy, such as rotational energy, vibrational energy, and



**INFLUENCE OF TEMPERATURE ON REACTION SPEED**—As the temperature rises, molecules of water (the large spheres in the illustration are the oxygen atoms; the small ones are hydrogen atoms) increase their speed and thus the frequency with which they collide.

4a

4b



4c

**THREE WAYS OF STORING ENERGY INSIDE MOLECULES**—Illustration 4a shows a polyatomic molecule. Part of the energy stored in it is due to the speed with which it moves in a straight line. It is said to consist of translational energy.

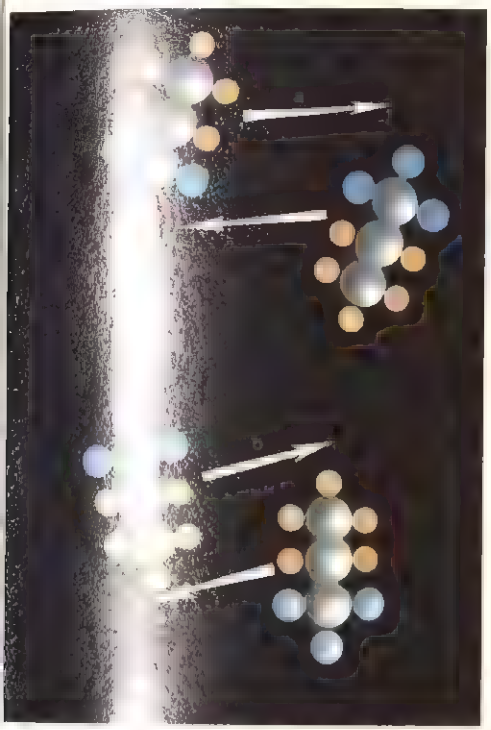
Illustration 4b is a diatomic molecule. It can be imagined as a pair of atoms held together by a spring, in which the two atoms can vibrate around the position of equilibrium. When two such molecules collide, part of the translational energy is transferred to the vibration. This type of energy is known as vibrational energy.

Another diatomic molecule is shown rotating in illustration 4c. If it collides with another molecule its rotation may be slowed and if it is accelerated it will then contain a greater quantity of the type of energy known as rotational energy.

**COLLISION BETWEEN TWO DIATOMIC MOLECULES IN ROTATION**—Even if two molecules are in slow movement when they collide, the impact between their touching parts will still be violent because they are rotating in the manner shown here.

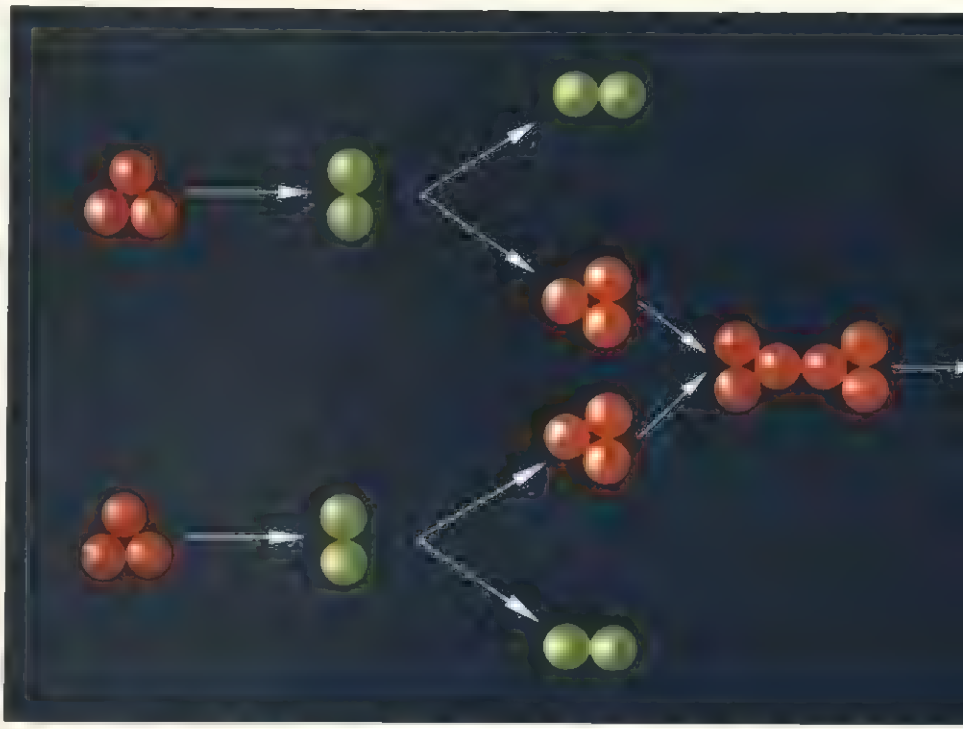
5

6



**STER** **FECT**—In the case of many mole-
cules collision does not indiscriminately
trigg action. The parts of the molecules
that nto contact with each other must
be t favor the development of the
reac s is known as the steric effect.
Illus shows the collision of two like
mole ithout a reaction occurring; the
same olecules, positioned as shown in
Illus 6b, would react on collision.

7



**CATALYSTS**—Catalysts are substances that initiate a reaction without taking part in it. Their effect is somewhat as shown here. Two triatomic molecules (red) would not react if they came into direct contact with each other. If, however, they collide with two molecules or atoms of a catalyzing substance before coming into contact with each other, they undergo internal transformations that will cause them to react if they touch. Throughout the reaction, the catalysts themselves remain unaltered, or are returned to their original form. Catalysts modify the reaction speed without being altered.

kine nergy. What happens, then, is that ecules involved in a collision acqu certain quantity of energy that is th distributed (how this occurs is not known) among the various coordinates of kinetic energy, rotational energy, and vibrational energy. However, only one particular distribution of energy, of all those possible, can cause the molecule to react. (Imagine, for example, three Cartesian axes inside each molecule, axes among which the energy is shared out.)

## EXPLOSIVE REACTIONS

The actual development of a reaction may in special circumstances bring about the very conditions that accelerate it. An example of this is the rapid increase in pressure that takes place during the decomposition of a substance such as nitroglycerin, causing the decomposition of molecules adjacent to others already decomposed. The propagation of the phenomenon of decomposition takes place so quickly that the reaction is said to be explosive. This type of reaction is not only typical of so-called explosive substances; it may also occur with other substances considered perfectly innocuous.

## REACTIONS BETWEEN HETEROGENEOUS PHASES

The laws governing the development of these reactions are difficult to determine, in that they depend on many factors. Without going too deeply into the subject, it should be mentioned that the speed at which these reactions develop depends not only on many of the factors affecting homogeneous-phase reactions but also on the extent of the contact surface between the two reacting substances. The speed at which coal burns, for example, depends on how much of its surface is in contact with the air, which is why breaking coal into small pieces (the smaller the better) causes it to burn quicker.

In the case of the solid propellant charges used in rockets, the speed at which combustion travels through the exposed surface of the charge is extremely critical in performance calculations. If the burning area increases, the rocket thrust increases; if the burning area decreases, the thrust decreases. Either condition—progressive burning and regressive burning, respectively—may be desirable; or, neutral burning, in which the speed of combustion and the amount of propellant consumed are constant, may be desired. In any case, speed of combustion depends on how much area of the combustible substance—the propellant—is in contact with the air as combustion proceeds: this speed is predetermined by the shape of the charge.

# VALENCE | the combining capacity of atoms

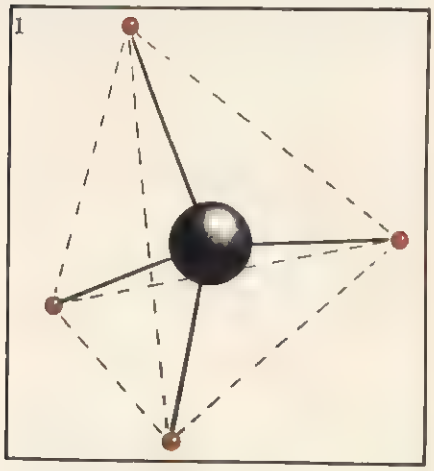
In a gas composed of atoms floating through space, the atoms react with each other only by accident, when they collide. The familiar material world presents quite a different picture. The universe consists to a large extent of relatively compact objects; the Earth is no exception. Most of the atoms of the Earth are closely packed together to form an almost spherical mass.

What forces govern the world of matter and bring order out of chaos? In most cases these forces involve action-at-a-distance. Each atom exerts an influence on its neighbors inside a certain radius. Thus, there is some degree of "communication" between atoms. This communication often takes the form of chemical bonds, in which chemical union occurs between atoms.

Considered in isolation, every atom has this combining capacity, which is referred to as an atom's valence in relation to other atoms. The term *valence* is used when combining capacity is discussed in quantitative terms. An atom of carbon (C), for example, is capable of bonding with four atoms of hydrogen (H) to form the methane molecule ($CH_4$). Thus, carbon is said to have a valence of 4, with respect to hydrogen for the methane molecule.

The aggregates of particles formed the chemical union of atoms vary co erably in size. The smallest of thes the molecule of gaseous hydrogen, wh consists of two atoms ($H_2$), whil quartz crystal ($SiO_2$) is an aggregat indefinite extent. Each atom of sili a quartz crystal is located at the c of a tetrahedron, the vertices of w

1



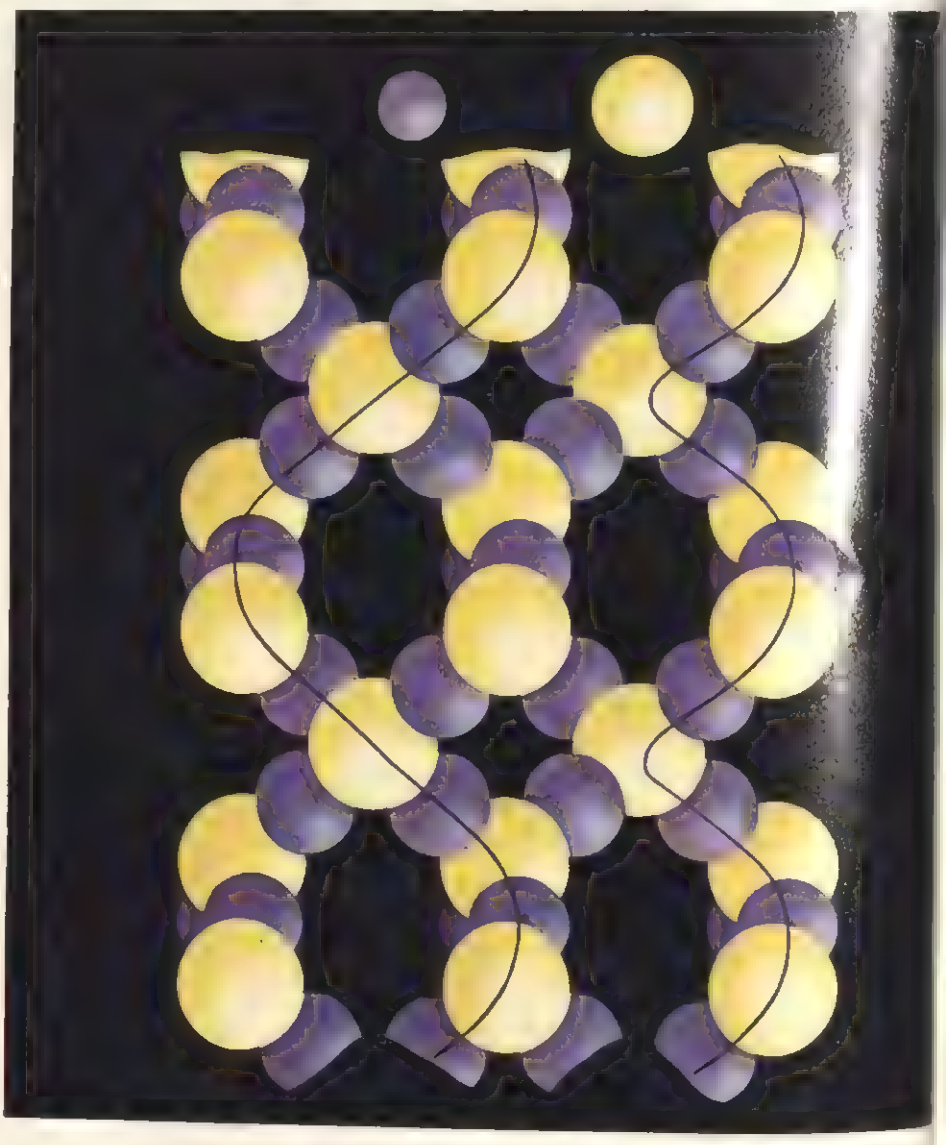
**METHANE MOLECULE**—The carbon atom is surrounded by four hydrogen atoms, and joined to them by single bonds. The hydrogen atoms each occupy the vertices of a regular tetrahedron (dotted line), at the center of which lies the carbon atom.

2

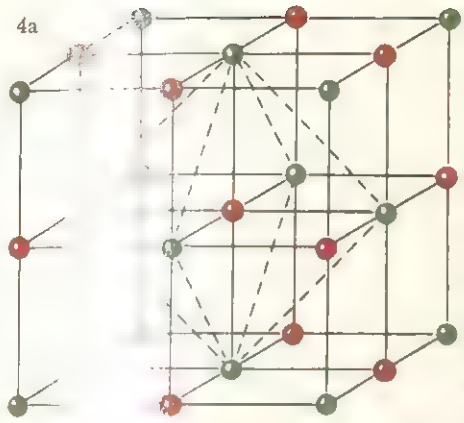
**HYDROGEN MOLECULE**—Two hydrogen atoms joined by a covalent bond make up the gaseous hydrogen molecule.

**BETA QUARTZ**—Each atom of silicon (violet) in a crystal of quartz ($SiO_2$) is located at the center of a tetrahedron. The vertices of these tetrahedra are occupied by oxygen atoms (yellow). Each of the oxygen atoms is then mon to another tetrahedron, and so on thr out the crystal.

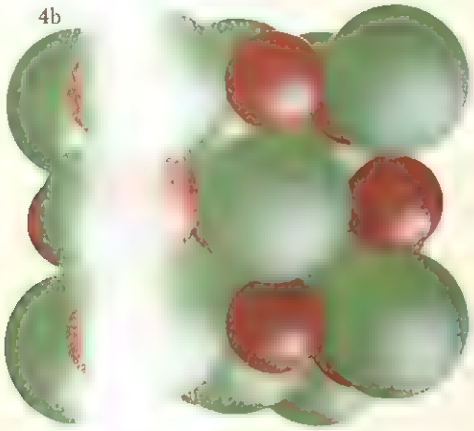
3



4a



4b



**SODIU[M] [CHL]ORIDE (COMMON SALT)**—This diagra[m] [sh]ows the perfectly symmetrical structure o[f] [a] crystal of common salt. Each atom of sod[ium] (blue) is surrounded at equal distances [by] six atoms of chlorine (green). Similarly, e[ach] atom of chlorine is surrounded by six ato[ms] of sodium, again at equal distances (illustr[ation] 4a). Illustration 4b shows the relative siz[es] of the ions in the NaCl crystal lattice.

are occupied by atoms of oxygen. Each oxygen atom, however, is part of an adjacent tetrahedron. This sharing extends throughout the crystal (a quartz crystal with a volume of 1 $mm^3$ contains millions of tetrahedra, each one linked to the next).

The term *molecule* is generally used to describe aggregates of atoms in which the bonding forces between atoms more or less are equal. These forces are known as interatomic forces. Examples include the forces between carbon and hydrogen in the methane ($CH_4$) molecule, between hydrogen and hydrogen in the gaseous hydrogen molecule ($H_2$), and between silicon and oxygen in a quartz crystal ($SiO_2$). By the terms of this definition a quartz crystal should by rights be regarded as a perfect example of a molecule. It is more usual, however, to use the expression "molecular structure" when a molecule is of these proportions.

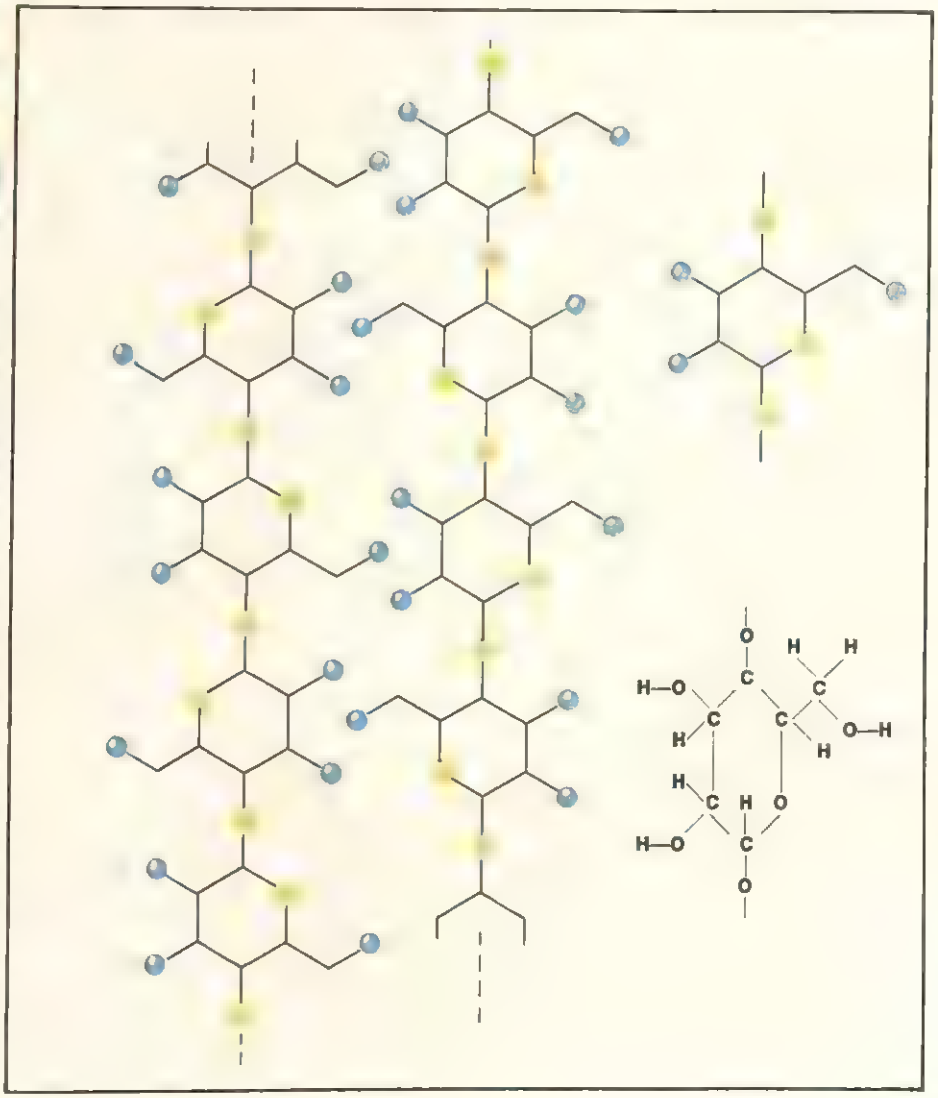
In many cases the chemical formula of a compound will give a clear idea of the structure of its molecule (methane, $CH_4$, for example). This does not always hold true, however. A formula such as $SiO_2$ (quartz) might suggest an equally simple molecule consisting of an atom of silicon surrounded by two atoms of oxygen, but this is not the case. Chemical formulas often fail to give an adequate description of molecular structure, which is frequently quite complex.

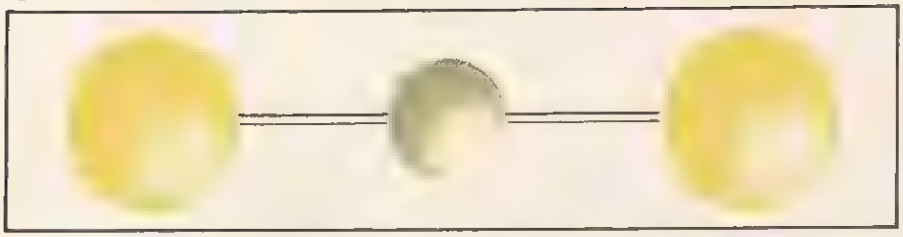
The combining capacity of the atoms of a molecule does not come to an end when the molecule is formed. Molecules can also link up with each other. The forces that make this possible, called intermolecular forces, are weaker than interatomic forces. The difference between the two types of force is one of degree only. There is no sharp dividing line between them.

Cohesion and rigidity in solids are sometimes the result of strong interatomic forces. This is the case with quartz and also sodium chloride (NaCl), in which every atom of sodium is surrounded at equal distances by six atoms of chlorine

**CELLULOSE IN A SHEET OF PAPER**—Arranged in long chains, the molecules are held together by intermolecular forces. Each chain is flanked by others of the same kind, with intermolecular bonds forming the links between chains and giving the paper its characteristic properties.

5





**CARBON DIOXIDE**—The molecule is formed of one atom of carbon (gray) and two atoms of oxygen (yellow). The carbon atom is joined to each oxygen atom by a double bond.

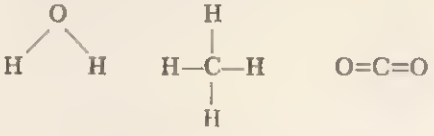
(and vice versa). The result is a perfectly symmetrical structure.

In other cases the stability of a solid is due to intermolecular forces between neighboring molecules. A sheet of paper, for example, owes its compactness and structural integrity to the intermolecular forces at work between individual molecules of cellulose. It is bonds of this sort that are broken when a piece of paper is torn, the weaker bonds reaching the breaking point first.

## VALENCE SATURATION

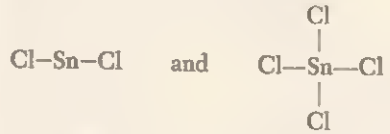
In the example of methane ($CH_4$), carbon has a valence of 4 with respect to hydrogen; each atom of carbon is surrounded by four atoms of hydrogen. In carbon dioxide ($CO_2$), each atom of carbon is surrounded by two atoms of oxygen, and it might be concluded that the valence of carbon with respect to oxygen is 2 in carbon dioxide. Since no compounds exist in which one atom of carbon has more than four atoms of hydrogen or more than two atoms of oxygen around it, however, it must be deduced that the bonding potential of carbon is "saturated" equally well by four hydrogen atoms or two oxygen atoms. Thus, 4-H and 2-O, or, in terms of proportion, 2-H and 1-O, must somehow be "equivalent" in their capacity to saturate carbon.

This equivalence is found also with respect to atoms other than carbon, especially in water ($H_2O$). These and other considerations involving many different types of atom led historically to a model of valency. Each atom is thought of as having a certain whole number of valencies capable of being saturated by an equal number of valencies from other atoms. To put it metaphorically, each atom has a certain number of "hooks" that interlock with the hooks of other atoms (Illustration 7). Hydrogen, for example, is said to have a valence of 1, since there are no compounds in which hydrogen is bonded to more than one atom (there are exceptions to this rule, but they do not alter its meaning). Oxygen, on the other hand, has a valence of 2; in water ($H_2O$), the oxygen atom is saturated by two atoms of hydrogen. Carbon has a valence of 4, which may be saturated by four univalent hydrogen atoms or by two bivalent oxygen atoms:



The bond between two atoms is said to be a single bond if there is one attachment "hook" (or valence) for each atom (as in water and methane), and a double bond if there are two hooks (or valences) for each atom (as in carbon dioxide); triple and quadruple bonds are also known.

Every atom has either one or more valences capable of being saturated. Sodium, for example, always has a valence of 1, whereas tin may have valences of 2 or 4. Tin thus forms two series of compounds—tin(II) and tin(IV). In the chlorides of tin, where the chlorine is univalent, two compounds exist:



tin(II) chloride tin(IV) chloride

## ELECTROVALENCE

Certain compounds exhibit the capacity to split up in solution into charged particles (ions). Positively charged ions are called cations and negatively charged ions are called anions. This phenomenon led to the concept of electrovalence. An ion is an atom or a group of atoms that has lost or gained a certain number of elementary negative charges (electrons). Ions are thus no longer neutral particles. To make the concept of electrovalence clearer, suppose that a chloride ion has a negative charge ($Cl^-$) and that a potassium ion has a positive charge ($K^+$). This can then lead to the formation of a neutral ion-pair of potassium chloride ($KCl$) through the union of these ions. The bonding force is electrostatic attraction between the oppositely charged ions.

According to this theory, no element is positive or negative in absolute terms, but may be located in a series including the atoms of all the other elements. Each atom in the series is positive with respect to the elements that follow it and negative with respect to the elements that precede it. Thus hydrogen is positive with respect to oxygen and negative with respect to sodium, while oxygen is negative with respect to hydrogen and positive with respect to fluorine.

| $1^+2^-$ | $1^+1^-$ | $1^+2^-$ |
|---|---|---|
| $H_2O$ | $NaH$ | $Na_2O$ |

Chemists have been able to work out a table showing the common electrovalences of the elements, positive electrovalences being referred to oxygen and negative electrovalences to hydrogen.

## WHERE THE CLASSIC THEORY OF VALENCE FAILS

The theory of valence summarized above has little more than a qualitative value. It fails to offer more than practical rules for the most common instances where atoms form bonds with each other. The theory brings a certain amount of order to a collection of apparently heterogeneous facts (historically, this is exactly how the theory developed). It must be remembered, however, that the real nature of the chemical bond is found in the electronic structure of bonded atoms.

The "hook" theory of valence is clearly inadequate when the stable carbon-oxygen compounds carbon monoxide ($CO$) and carbon dioxide ($CO_2$) are considered. In the former the carbon valence

seems to be only partially saturated. The theory does not explain why any other compound in which the valences of an atom are only partially saturated should be stable. Nor is the concept of electrovalence capable of covering all phenomena connected with valence. Stable molecules formed of equal atoms do in fact exist. Gaseous chlorine ($Cl_2$) is a case in point, as is gaseous hydrogen ($H_2$), to say nothing of equally stable molecular solids consisting of a single element (metals, diamond, and so forth). If bonds between equal atoms do exist, they cannot be the result of attraction between opposite charges, for the constituent atoms clearly have equal charges of the same sign. In a great many cases electrovalence is no more than a theoretical aid in checking the saturation of the valences of the atoms in a compound.

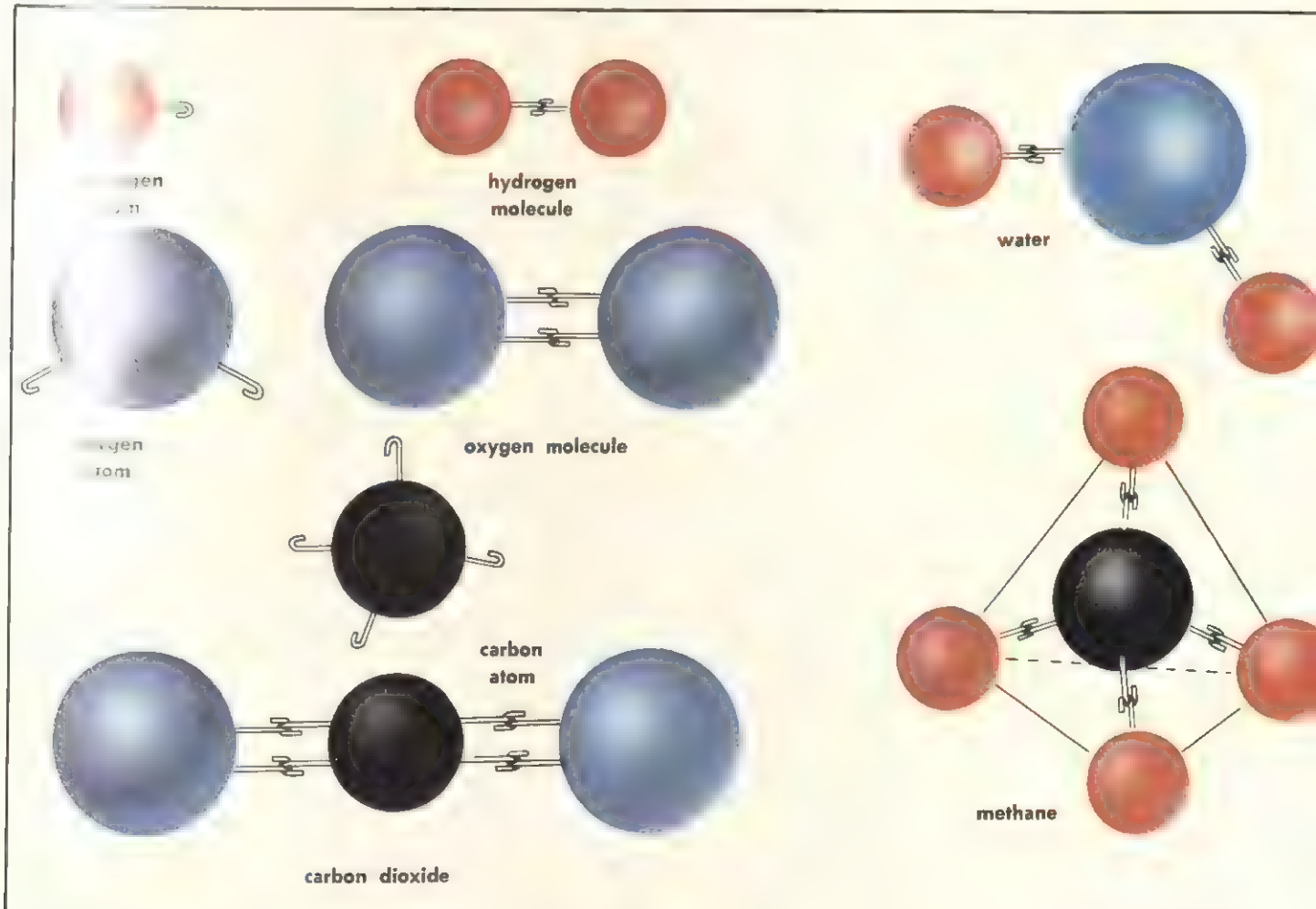
## COVALENCE

Another kind of valence of great importance is covalence, which results from the sharing of two electrons by two atoms. The bond that consists of a pair of shared electrons is called a covalent bond; it is represented by a dash in organic structural formulas. A covalent bond between two atoms consists of two electrons occupying one orbital for each atom. Hydrogen, $H_2$, is a simple example of a covalent molecule.

The number of atoms surrounding any given atom in a compound is called the coordination number of that atom. Useful though this concept was for preliminary quantitative conclusions on valence, it is now essential to correct the impression that valence and coordination number are one and the same thing. It frequently happens, especially in solid compounds, that the coordination number differs, sometimes widely, from the valence. In the case of common salt, each $Na^+$ ion is surrounded by six $Cl^-$ ions, but the valence is one. In the case of individual molecules of sodium chloride in the gaseous state, however, electrovalence and covalence do indeed coincide; that is, one sodium ion and one chloride ion are combined in a single molecule.

**ATOMS AND THEIR "HOOKS"**—Every atom is equipped, metaphorically speaking, with a certain number of hooks that enable it to grasp other atoms. Hydrogen has only one (in other words, a valence of one), while oxygen has two, which can be saturated by two hydrogen atoms. Carbon has four valence sites, which can be saturated by four hydrogen atoms, as in methane ($CH_4$), or by two oxygen atoms, as in carbon dioxide ($CO_2$).





# CATALYSIS | the governing of chemical reactions

To some extent, all chemical reactions tend to go to completion, forming products from the reactants. Naturally, some of these reactions are extremely rapid—for example, water formed from hydrogen and oxygen. Many reactions, however, proceed very slowly—too slowly to produce desired yields in a reasonable amount of time. For reactions of this type, a material can be added that speeds up the process, and such a material is called a catalyst.

Catalysts are substances that alter reaction speeds while themselves remaining unchanged. In fact, a catalyst introduced into a reaction at its inception should be totally unchanged as to nature and amount on the completion of the reaction.

Essentially of two types, catalysts are classified as positive when they accelerate reaction speed and negative when their effect is to slow down a reaction. Positive catalysts find by far the greatest application both in the laboratory and industrially. In either case, it is essential to have a knowledge of the events taking place in a chemical reaction.

The speed of a reaction is in direct proportion to the concentration of the reactants. Thus, altering the concentrations has an effect on the rate at which the reaction goes to completion. However, if it is impractical or unwise to change the concentrations of the reactants, then the rate must be changed. But how?

In chemistry, the rate (or speed) of a reaction is expressed as the constant, $k$. To determine the value of $k$, the following equation (called Arrhenius' equation after its postulator) is used: $k = A^{-E/RT}$. In the equation, $A$ represents the number of collisions of reacting species (the so-called frequency factor), $R$ the gas constant (derived from physical laws), and $T$ the absolute temperature. The energy—often called the activation energy—required for the system to overcome its inertia is expressed as $E$. The latter is an expression of the energy needed for the reaction to occur, and is measured in kcal/mole.

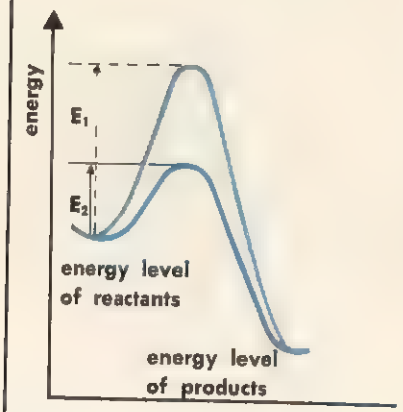
The rate of a reaction can be increased by changing the values of either $E$ or $T$. However, it is not always possible to increase the temperature; therefore, this necessitates a decrease in the energy put into the system. Also, the frequency of collisions of the reactants can be modified, changing the value of $A$. In both instances, the desired results can be achieved by using catalysts.

One effect of catalysts is to cause reactions to pass through intermediate stages with values for $E$ that are lower than in similar noncatalyzed reactions. As graphed in Illustration 1, this results in an increased rate $k$. Another effect produced by catalysts such as activated carbon is an increase in the number of ionic or molecular collisions. Alteration of the value of $A$ to a higher frequency carries with it a change in the speed of the reaction.

Theoretically, a catalyst should come out of the reaction in the same state in which it was introduced. Sometimes, however, trace impurities in the reagents inhibit catalytic action through adsorption by or reaction with the catalyst. This problem, called catalyst poisoning, is solved by using highly purified reagents, or by periodic reactivation of the catalyst through processes specific to the poison.

Although catalysts are widely used, their mechanism is not completely understood. However, catalysis is considered to be homogeneous (when both catalyst and reagents are in the same phase) or heterogeneous (when each is in a different phase). Various mechanisms have been suggested for each type of catalysis, but only recently have attempts been made to develop a unified theory.

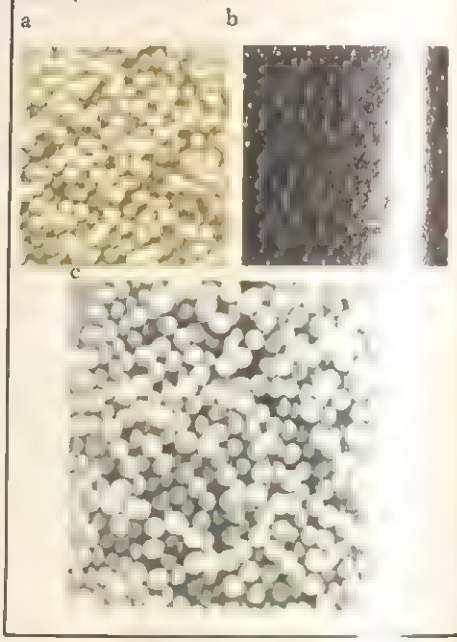
1




**CATALYTIC REACTIONS**—Catalysts lower the energy barrier between the reagent state and the product state. As the graph in this illustration indicates, the energy requirement $E_1$ of a noncatalytic reaction is relatively higher than that of a catalytic reaction $E_2$.

2

**PLATINUM ON ALUMINA**—Platinum is used as a catalyst in the refining of petroleum to make gasoline. Illustration 2a shows the unused, highly active catalyst, while Illustration 2b shows the same catalyst after three months of use; in this state, it is inactive. However, regeneration transforms it back into a useful state (Illustration 2c).




## HOMOGENEOUS CATALYSIS

The term "homogeneous catalysis" can be applied only to those reactions in the gaseous or liquid phase, where all components are in a similar state.

A reaction between gases occurs only when the reagent molecules collide with one another. It is axiomatic that for such reactions to occur, a definite quantity of energy must be available to the system. The presence of a catalyst does not change this fundamental mechanism. It will, however, allow the formation of a series of intermediate compounds whose energy requirements are less than those of the reaction as a whole.

One of the best-known and most important examples of a gas-gas catalytic reaction is the oxidation of sulfur dioxide, $SO_2$, to sulfur trioxide, $SO_3$; the latter is used in sulfuric acid production. This reaction is catalyzed by the presence of nitric oxide, NO, which acts as an oxygen carrier:

$$2NO + O_2 \rightarrow 2NO_2$$
$$NO_2 + SO_2 \rightarrow SO_3 + NO.$$

This is a relatively direct type of reaction whose speed is proportional to concentration.

A second version of a gas-gas catalytic reaction, this time requiring a chain of reactions for completion, is the oxidation of carbon monoxide in the presence of water vapor. Although the mechanism of

this reaction has not been fully explained, one logical assumption is:

$$CO + H_2O \rightarrow CO_2 + 2H$$
$$2H + \tfrac{1}{2}O_2 \rightarrow H_2O.$$

It would appear that the water vapor acts as an oxygen carrier. However, the mechanism could also involve the following chain:

$$H_2O + O_2 + CO \rightarrow CO_2 + 2OH$$
$$(\quad) \rightarrow CO_2 + H$$
$$H + O_2 + CO \rightarrow CO_2 + OH.$$

In this case the effect that the wall of the container has on molecular collisions may be questioned. If wall effects occur, this reaction cannot be a truly homogeneous catalysis. Another point to consider is that carbon monoxide is easily oxidized in the absence of water vapor. Nonetheless, this process provides a reasonable look at what might occur in a chain type gas-phase catalytic reaction.

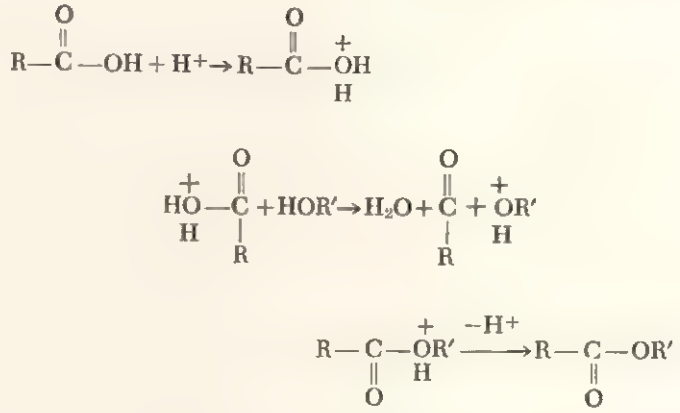
In the liquid phase, reactions are generally slower than those encountered between gases, hence, a greater need for catalysts.

Reactions in the liquid phase that are catalyzed by the presence of acids or bases are examples of homogeneous catalysis. Studies of these reactions have demonstrated that the ions act as the catalytic agents. In fact, in certain reactions (the hydrolysis of esters, for example) a distinct correlation appears to occur between hydrogen ion concentration and catalytic activity.

Generally, the reactions catalyzed by acids or bases are characterized by proton transfer. In acid catalysis, this transfer is from catalyst to reagent, while this direction is reversed in basic catalysis. This proton transfer leads to the formation of intermediate products with lessened energy requirements and a proportionate increase in reaction speed. Reactions of this type are especially important in organic synthesis.

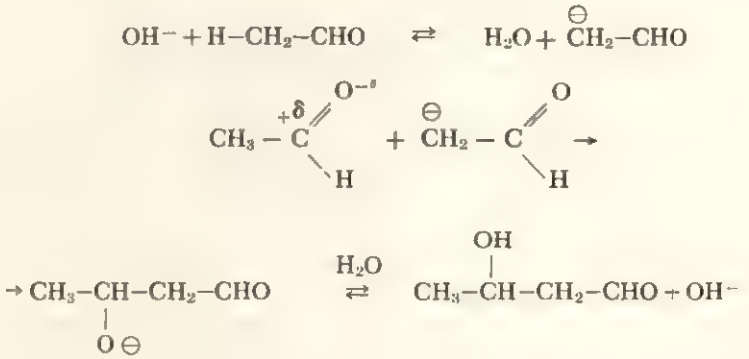
An example of acid catalysis is provided by the esterification of primary and secondary alcohols, a common organic reaction. In this reaction, a proton from the mineral acid accepts an unpaired electron from the alcohol. This, in turn, leads to the formation of an ion not unlike that which water forms with $H^+$ cations. This newly formed ion is reacted on by the alcohol, forming both water and an ester. The following reaction also recreates the proton that is required in order to begin the process all over again:

a



Basic catalysis and its mechanism are illustrated in the condensation reaction of an aldehyde, one of organic chemistry's most important reactions:

b



## HETEROGENEOUS CATALYSIS

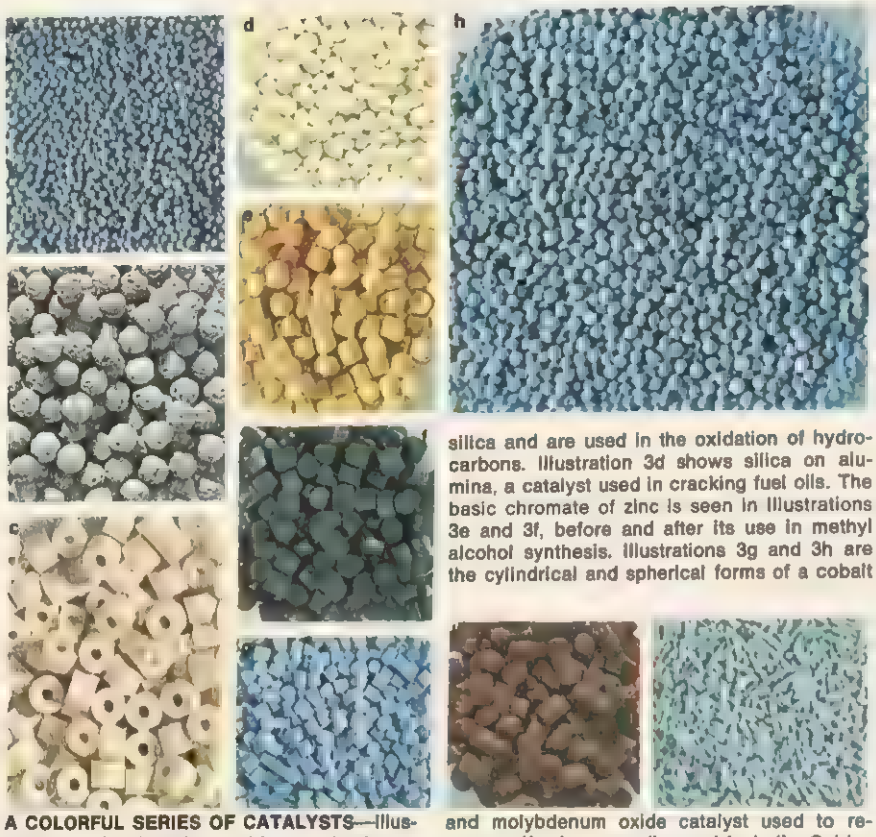
In catalytic reactions of the heterogeneous type, the catalyst is in some phase other than that of the reacting system. Normally, the catalyst is a solid, thus forming a solid-gas, solid-liquid, or solid-solid system with the reactants. However, when referring to heterogeneous catalysis, chemists invariably mean a solid-fluid system, in which the term "fluid" incorporates both gases and liquids.

It was once thought that catalysis in a solid-gas system was due exclusively to the adsorption phenomenon, the concept being based on the concentrations of the reagents at the surface of the solid. With the concentration so controlled, molecular collisions would be greatest and the reaction rate proportionately accelerated. However, subsequent research determined that catalytic activity was not proportional to adsorption. This led to the hypothesis that the reaction of two gases catalyzed by a solid is, first, adsorption at adjacent points on the surface of the solid. Then, assuming sufficient energy, the reactants form intermediate compounds with surface atoms of the catalyst, these compounds rapidly decomposing to form the products.

The work behind this hypothesis also showed that a catalyst is not equally active over its entire surface, but that the catalytic action was confined to activity centers on the surface. These centers are thought to consist of atoms situated at the vertices and corners of surface crystals, since these atoms possess residual charges. Further, the number of activity centers increases in proportion to the irregularities in the catalyst's crystalline lattice. This last point indicates the usefulness of increasing the specific surface area of a catalyst as much as possible. This is accomplished by using finely divided agents as opposed to solid masses.

Certain substances, called promoters,

3




**A COLORFUL SERIES OF CATALYSTS**—Illustration 3a is chromium oxide on alumina, a catalyst used in dehydrogenating saturated hydrocarbons. The spheres in illustration 3b are used in oxidizing ethylene to ethylene oxide, and consist of silver on alumina. The pierced cylinders in illustration 3c are composed of bismuth and molybdenum oxides on silica and are used in the oxidation of hydrocarbons. Illustration 3d shows silica on alumina, a catalyst used in cracking fuel oils. The basic chromate of zinc is seen in illustrations 3e and 3f, before and after its use in methyl alcohol synthesis. Illustrations 3g and 3h are the cylindrical and spherical forms of a cobalt and molybdenum oxide catalyst used to remove sulfur from gasoline and fuel oils. Oxides of iron, chromium, and potassium (illustration 3i) are catalysts in the hydrogenation of ethyl benzene into styrene and of butane into butadiene, while nickel and molybdenum oxides on alumina (illustration 3j) are widely used in many hydrogenation reactions.

are capable of reinforcing the activity of catalysts to which they are added. Although such materials do not perform any direct catalytic action, they can deform the crystal lattice to increase its surface; they can prevent the aging of the catalyst and prolong its useful life; or they can actually alter the catalyst's surface structure. One such promoter is alumina.

A characteristic example of heterogeneous catalysis is seen in the synthesis of nitric oxide through oxidation of ammonia:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O.$$

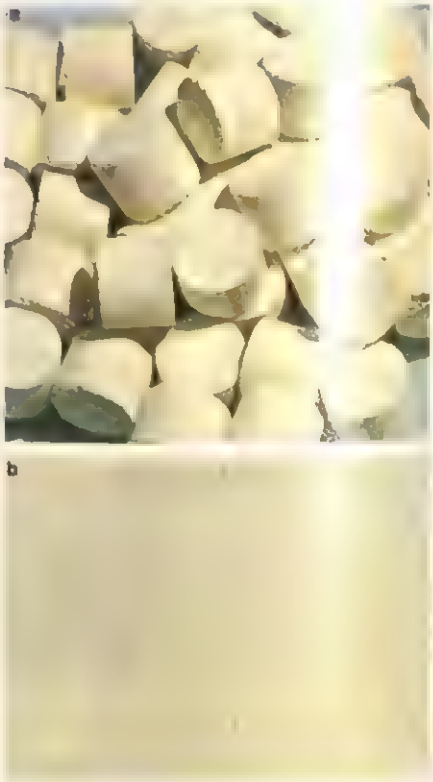
In this reaction, the catalyst is platinum in the form of a mesh through which the reacting gases are passed. When the platinum is new, the yields are relatively low. As the mesh becomes etched and the wires develop irregularities through use, however, the product formation increases simply because the surface area and activity centers of the catalyst have increased.

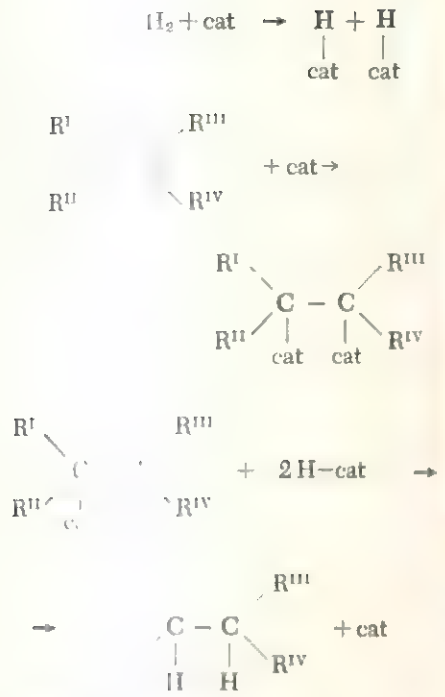
In the nitric oxide process, platinum catalysts are essential. In other instances, however, this material is unsuitable. For example, in the hydrogenation of coal tars, platinum would be converted to its sulfide by the sulfur contained in the reactants, rendering it inactive. Thus, tin and tungsten sulfides are used to catalyze these reactions because of their immunity to the action of sulfur.

One of the chemical industry's most important reactions is that of hydrogenation. This involves the destruction of double bonds in unsaturated hydrocarbons and the subsequent formation of the saturated hydrocarbons. Two metal catalysts used in this type of reaction are an alloy—Raney nickel—and carbon palladiate. Such catalysts perform the simultaneous functions of reacting with molecular hydrogen to break the single H–H bond and with unsaturated hydrocarbons to break the double C=C bond. Once this is accomplished, reactions can occur that lead to the formation of saturated compounds called alkanes. Schematically, these reactions are:

4

**THE CATALYST FOR ACRYLONITRILE**—The cylinders in illustration 4a and the powder in illustration 4b consist of vanadium, molybdenum, bismuth, and silica, and constitute suitable catalysts for making acrylonitrile ($H_2C=CHCN$), a raw material used in making acrylic rubber and fibers.





NEGATIVE CATALYSIS

For the most part, catalysis is thought of as increasing the speed of reactions. Certain other reactions, however, require some method of slowing the speed of a reaction, and in such cases the so-called negative catalysts are used. They are employed, for example, when it is necessary to inhibit a side reaction in favor of the principal reaction. This practice is quite common in organic chemistry, where numerous reactions take place simultaneously. Such an example is provided by manganese. In the form of its 2+ ion, manganese has the negative catalytic effect of slowing the oxidation reaction between acetaldehyde and acetic acid.

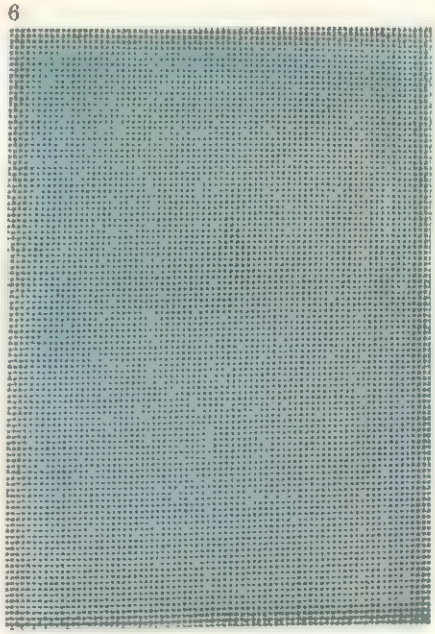
Negative catalysts are sometimes used as stabilizers, and as such are added to materials that would otherwise rapidly undergo deterioration. For example, chloroform is readily converted to toxic phosgene ($COCl_2$) in the presence of light and air. The addition of a small percentage of ethyl alcohol stabilizes the chloroform, thus preventing this unwanted reaction.

**OXIDATION OF ETHYLENE TO ETHYLENE OXIDE**—Ethylene oxide is prepared on a commercial scale by use of the catalytic oxidation of ethylene by air. The catalyst is silver on alumina, and the reaction occurs at temperatures around 250° C (482° F):

Illustrations 5a and 5b show the catalyst in two forms.

**PLATINUM MESH**—Because platinum adsorbs oxygen under certain conditions, as when fine wire is woven into a mesh, it is an effective catalyst. In the form seen here, the metal is used in synthesizing nitric oxide from ammonia, the basis for the manufacture of nitric acid.

6



**RANEY NICKEL AND CARBON PALLADIATE**—Raney nickel is obtained by treating an aluminum-nickel alloy with hot sodium hydroxide. Because it is a pyrophoric compound, it is stored under alcohol in the flask. The powder on the watch glass is carbon palladiate.

7

# CHEMICAL REACTIONS | from reactants to products

A chemical reaction is that process in which two or more elements or compounds combine, giving rise to a substance or substances of a different character. The materials entering into combination are called reactants (or reagents), while those formed as a result of the reaction are called products. In the simplest of terms, chemists think of a chemical reaction as a series of events in which reactants yield products. In any reaction, it is fundamental to understand that the products are totally influenced by the nature of the reactants and by the type of reaction in which they are formed. Thus—without going into elaborate detail—sunlight causes components in human skin to form vitamin D while in plants the same sunlight starts a reaction that leads to the formation of sugars.

In order to represent chemical reactions, a system of chemical shorthand has been devised. In this way, the events in a reaction can be compared to a mathematical equation consisting of two parts. The first part represents the amounts of the various reactants and the second part does the same for the products. Quantitatively, amounts are stated as the number of atoms, ions, or molecules required of reactants and products in any given equation. The substances, themselves, are expressed by their chemical symbol (in the case of atoms, ions, and certain molecular atoms) or by their chemical formula (in the case of molecules and for ions containing more than one element). Instead of the usual equal sign common to mathematics, an arrow separates the two halves of a chemical equation. Generally, the arrow points in the direction of the products, from left to right. There are equations, however, that use a double arrow, or a set of arrows, indicating that the reaction goes in both directions. This is easily clarified by considering two reactions, the first requiring a single arrow only:

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl.$$

Here, the reaction between barium chloride, $BaCl_2$, and sulfuric acid, $H_2SO_4$, can lead only to the formation of barium sulfate, $BaSO_4$, and hydrochloric acid, HCl. In other words, the reaction goes to completion because it continues until one of the reactants is used up. The left-to-right arrow also says that a reverse reaction is not possible under the same conditions. That is, no reaction will take place between barium sulfate and hydrochloric acid to yield barium chloride and sulfuric acid.

Now consider the reaction between hydrogen and iodine in the formation of hydriodic acid:

$$H_2 + I_2 \rightleftarrows 2HI.$$

In this case, a double arrow is required to indicate a reaction that does not go to completion. Rather, the reactants and the product tend to reach a state of equilibrium determined by their respective concentrations at a given temperature. Such an equilibrium reaction will continue going backward and forward as long as conditions in the system stay constant.

Whether or not a chemical reaction goes to completion or tends to reach equilibrium, there are precise conditions that must be fulfilled if it is to be valid. First, the reaction, hence its equation, must represent a real process, one that will actually take place. There are many reactions that can be represented by an equation but that, in fact, cannot occur. Then the reaction must comply with Lavoisier's principle of mass conservation that states, in essence, that matter cannot be created or destroyed by ordinary chemical means. In other words, the atoms of the reacting substances must also be present in the molecules of the products in equal numbers.

Finally, a reaction must be "balanced" so that the electronic charge of the products is equal to the total charge of the reactants. Since the charges are expressed in terms of valence or oxidation state possessed by each element, it is relatively simple to determine the accuracy of a chemical equation. The key points to remember are, first, that the valence of an uncombined element is always equal to zero. The same value holds for a compound, in which the positive and negative oxidation states of its components cancel one another. Second, each element has at least one valency, and in a balanced chemical equation the sum total of all electronic charges on both sides of the arrow must equal zero.

As an example of an equation that meets all of the conditions for validity, consider the reaction between sodium hydroxide and hydrochloric acid:

$$NaOH + HCl \rightarrow NaCl + H_2O.$$

This reaction satisfies the reality condition because it does represent an actual

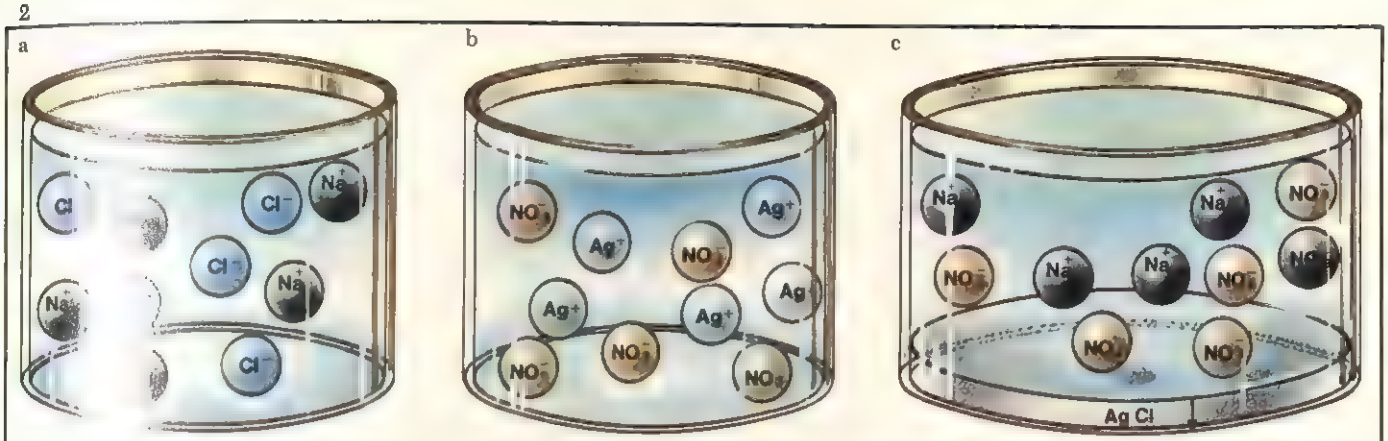
1

**CHEMICAL REACTIONS**—Chemical reactions can be classified into two general categories, one involving transfer of electrons and the other in which there is no variation in the oxidation state of the elements. Of the reactions occurring in aqueous solution, most belong in the latter classification, and some of these are illustrated here. The reactions are represented in both molecular and ionic forms.

In representing a reaction in its ionic form, certain conventions are used: in the case of strong electrolytes the equations show only those ions actually taking part in the reaction; weak electrolytes and nonelectrolytes are written in molecular form; and substances that are either slightly soluble or are insoluble are shown underlined as molecules. Finally, if one of the products is a precipitate, it is indicated as such by an arrow pointing downward. But, if one of the products is a gas, an arrow pointing upward indicates this.

| | | | | | |
|---|---|---|---|---|---|
| $Bi(NO_3)_3$ bismuth nitrate | + $3NaOH$ sodium hydroxide | → | $3NaNO_3$ sodium nitrate | + $Bi(OH)_3$ bismuth hydroxide | $Bi^{+++} + 3OH^- \rightarrow \underline{Bi(OH)_3}\downarrow$ |
| $FeS$ iron sulfide | + $2HCl$ hydrochloric acid | → | $FeCl_2$ iron chloride | + $H_2S$ hydrogen sulfide | $\underline{FeS} + 2H^+ \rightarrow Fe^{++} + H_2S\uparrow$ |
| $HCl$ hydrochloric acid | + $CH_3COONa$ sodium acetate | → | $CH_3COOH$ acetic acid | + $NaCl$ sodium chloride | $H^+ + CH_3COO^- \rightarrow CH_3COOH$ |
| $Al(OH)_3$ aluminum hydroxide | + $3HCl$ hydrochloric acid | → | $AlCl_3$ aluminum trichloride | + $3H_2O$ | $Al(OH)_3 + 3H^+ \rightarrow Al^{+++} + 3H_2O$ |

2




**THE F[illegible]ION OF SILVER CHLORIDE**—When [illegible]n of sodium chloride, containing bo[illegible]m and chloride ions (Illustration 2a[illegible]d to a solution of silver nitrate, in wh[illegible]are silver ions and nitrate ions (Illustra[illegible]), the result is the formation of silver chloride as a precipitate (Illustration 2c). Because of its solubility the other product, sodium nitrate, remains in solution as the component ions.

Expressing this reaction in the ionic form and eliminating those ions that remain unchanged, it is immediately apparent that the reaction consists only of the formation of the silver chloride as a precipitate:

$$Na^+ + Cl^- + Ag^+ + NO_3^- \rightarrow Na^+ + NO_3^- + AgCl\downarrow$$
$$Ag^+ + Cl^- \rightarrow AgCl\downarrow.$$

event. In this case, the reaction is the neutralization of an acid by a base (or vice versa) and all such neutralization reactions are valid. Next, Lavoisier's principle is observed because all the atoms found in the reactants occur in the products in equal numbers. Last, since true compounds are present in all cases the total electrical charge comes to zero by virtue of the negative charges effectively canceling one another.

Now examine the reaction between barium hydroxide and hydrochloric acid:

$$Ba(OH)_2 + HCl \rightarrow BaCl_2 + H_2O.$$

It is immediately apparent that something is wrong. In the reactants there are three hydrogen atoms, but only two in the products; there are two chlorine atoms in the products, but just one in the reactants; while there are two oxygen atoms on the left, there is but one on the right. The easiest way to balance this equation (or, for that matter, most equations) is to determine quantitatively from the products the number of atoms needed on the reactant side of the arrow. Obviously, there is a shortage of hydrogen and chlorine atoms. Thus, by multiplying the hydrochloric acid by a factor of two, this deficit is resolved. Now, however, there are one less oxygen and two less hydrogen atoms on the right; this is overcome by multiplying the water by two:

$$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O.$$

In real terms, this equation says that one mole of barium hydroxide reacts with two moles of hydrochloric acid to yield one mole of barium chloride and two moles of water. The term mole is chemical shorthand for the molecular weight of a compound expressed in grams. Therefore, 171.34 g of $Ba(OH)_2$ react with 72.90 g of HCl to form 208.24 g of $BaCl_2$ and 36.00 g of $H_2O$.

The mechanisms in chemical reactions are perhaps more easily understood if they are thought of in terms of reactant ions recombining to form product molecules. Generally, reactions can be classified as those that involve electron transfer and those that do not.

One of the most common reactions is that of neutralization in which one of the products is a salt and the other is water if the reaction is between an acid and a base. In fact, this type of reaction is the simplest method for producing a salt. For instance, when solutions of sulfuric acid and barium hydroxide are reacted, there is immediate precipitation of the salt, barium sulfate:

$$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O.$$

The reaction can be considered ended when further addition of acid does not result in the continued precipitation of the salt. Qualitatively, it can be said that neutralization is complete. However, on a quantitative basis it is impossible to pinpoint the reaction's end point simply by adding an excess of reagent until no more precipitation forms. If all that is desired is the precipitation of an ion in solution, the qualitative approach is sufficient. To determine the exact point at which total neutralization has occurred, however, requires special skills and equipment that incorporate systems sensitive to hydrogen ($H^+$) and hydroxyl ($OH^-$) ion concentrations.

In reactions between strong acids and strong bases it is important to note that the heat produced in the reaction will always be about 1,370 calories per gram equivalent of the reactants. This figure corresponds to the ionization heat of water expressed as a positive value. It is due to the fact that the salt is produced by a reaction in which water is formed, as shown by these ionic equations:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$$
$$Ba^{2+} + 2OH^- + 2H^+ + SO_4^{2-} \rightarrow Ba^{2+} + SO_4^{2-} + 2H_2O$$
$$K^+ + OH^- + H^+ + NO_3^- \rightarrow K^+ + NO_3^- + H_2O.$$

(Because of the intervention of other factors, these remarks do not apply to reactions between weak acids and bases.)

Other reactions in which salts are formed include those involving direct treatment of an oxide with an acid anhydride:

$$CaO + CO_2 \rightarrow CaCO_3;$$

or by treating a base with an acid anhydride:

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O;$$

or by treating an oxide with an acid:

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O.$$

Finally, salts can be obtained when an acid (or base) displaces another acid (or base) from one of its salts in what is called a simple exchange reaction:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$
$$AgNO_3 + HCl \rightarrow AgCl + HNO_3;$$

or by reacting two salts in a double exchange reaction:

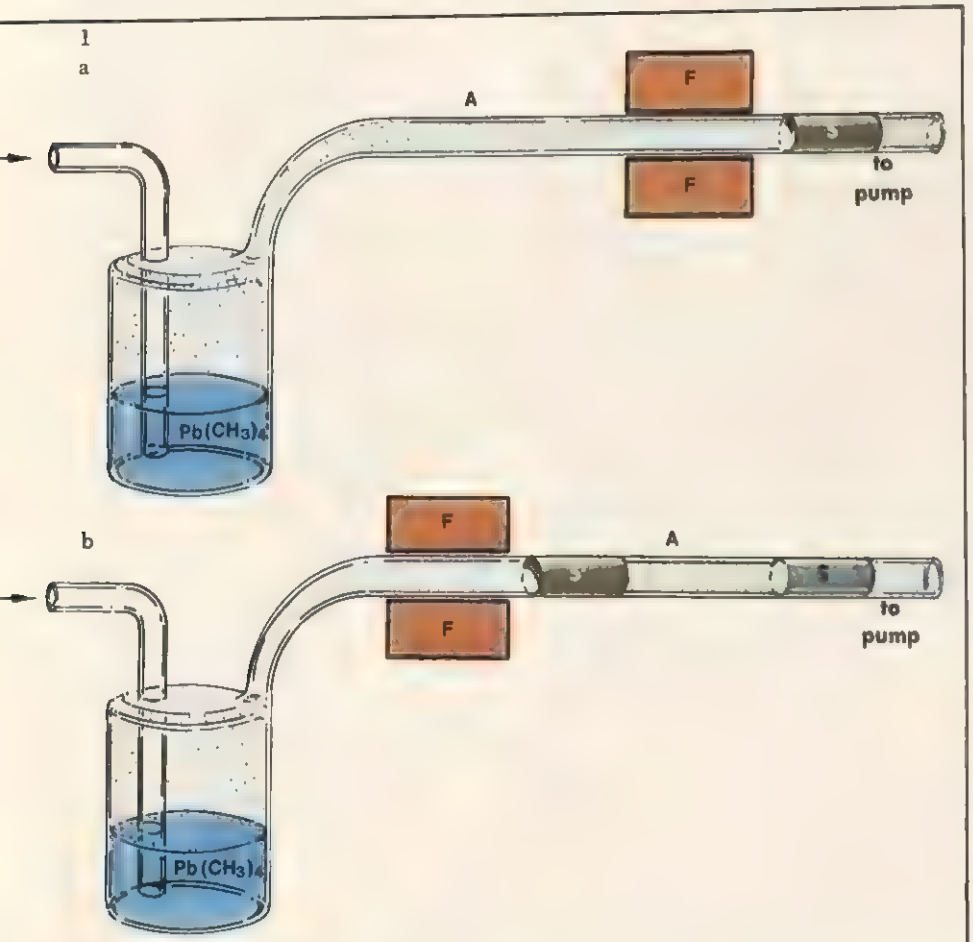
$$BaCl_2 + K_2SO_4 \rightarrow BaSO_4 + 2KCl$$
$$ZnSO_4 + BaS \rightarrow BaSO_4 + ZnS.$$

Simple and double exchange reactions are possible when they lead to the formation of insoluble compounds or to gases. In either case, by precipitation or escape, these products can be subtracted from the reaction; they no longer take part.

# CHEMICAL REACTIONS INVOLVING FREE RADICALS | one reaction can produce thousands

Chemical reactions can be rather simple affairs like the formation of water from hydrogen and oxygen, or they can be extremely complex such as the chemical reactions seen in human physiology. This does not mean, however, that complex reactions are confined to human physiology.

Occupying a place of considerable importance among the complex reactions are so-called chain reactions involving free radical intermediates. In such reactions, these intermediates are generated at some point and in turn create the conditions to continue the reaction. Thus, the products of this series of events result from a succession of elementary stages that are repeated on a well-defined periodic basis. It is believed that free radicals are transient intermediates in many high-temperature reactions, including combustion.




**PANETH'S EXPERIMENT**—The existence of free radicals was first demonstrated experimentally in 1929. Also called the "experiment of the mirrors," the experiment is shown in this illustration. Quite simply, a stream of nitrogen is saturated with tetramethyl lead and passed through a tube **A** (illustration 1a). At some point along the tube, the mixture is heated to about 500° C (932° F) by the furnace **F**. The result is the formation of a lead mirror **S** on the wall of the tube as it exits from the furnace. Moving the furnace to the left (illustration 1b), a second mirror is produced in the same manner as the first. However, while the second mirror **S'** forms, the first gradually disappears. This experiment shows that the tetramethyl lead decomposes according to the equation:

$$Pb(CH_3)_4 \rightarrow Pb + 4CH_3\cdot.$$

The metallic lead gives rise to the mirrors. The methyl radicals, in the second part of the demonstration, react with the lead in the first mirror to reform tetramethyl lead and subsequently to remove the original lead mirror deposits.

This experiment was later perfected to demonstrate that metallic lead could be reacted on by numerous organic materials through the creation of free radicals.

## FREE RADICALS

A free radical is defined as an atom or group of atoms containing at least one unpaired electron. This gives rise to an electrical instability, and distinguishes a free radical from a normal atom or group in which a stable situation exists in a manner similar to that of ions. The resulting electrical instability of a free radical imparts a strong tendency to react chemically. Unlike ions, however, free radicals are highly unstable, and this instability accounts for a high degree of reactivity.

Generally, free radicals are formed as a result of bond breakage in an otherwise stable molecule. It must be noted, however, that certain molecules have unpaired electrons—but these molecules cannot be considered free radicals. Molecules of this type are closer to what are considered ions.

Nomenclature indicates a free radical in much the same way as an ion, with the charge of the ion replaced by a dot. For example, these atoms or groups are all free radicals frequently encountered in chain reaction studies:

| | |
|---|---|
| $H\cdot$ | hydrogen atom |
| $Cl\cdot$ | chlorine atom |
| $Br\cdot$ | bromine atom |
| $OH\cdot$ | hydroxyl group |
| $CH_3\cdot$ | methyl group |
| $C_2H_5\cdot$ | ethyl group |

Kinetically, a reaction between a free radical and a molecule normally leads to the formation of other free radicals. This becomes clear with the understanding that a molecule, in most cases, has no unpaired electrons and that its charge is zero. Because a radical does have at least one unpaired electron, and because its tendency is to reach stability, in the process of taking electrons from molecules, products are formed that again contain unpaired electrons.

For example, if an atom of hydrogen (as a free radical) is reacted with a neutral molecule of bromine, the following occurs:

$$H\cdot + Br_2 \rightarrow Br\cdot + HBr.$$

The free radical bromine atom thus produced can, in turn, react with a hydrogen molecule:

$$H_2 \rightarrow H\cdot + HBr.$$

The reaction will continue in successive stages, setting up a chain reaction between free radicals and molecules until one or the other is used up.

In certain cases of chain reactions such as those just considered, as well as many others, a specific chain reaction agent gives rise to only one other such agent. Therefore, reactions of this type are defined as stationary chain reactions. However, each chain reaction agent can generate two or more free radicals. Reactions of this type are more than self-sustaining, and can build up rapidly. Such reactions are called ramified chain reactions.

## MAGNETIC PROPERTIES

Molecules with even numbers of paired electrons are slightly repelled by a magnet, while free radicals are attracted by a magnet. Because of the spin of the odd electron, the spins of the remaining paired electrons effectively cancel each other. Magnetic susceptibility tests may therefore be used to detect free radicals.



**CHAIN REACTIONS**—An extensively studied chain reaction is that between hydrogen and chlorine that leads to the formation of hydrogen chloride, represented in Illustration 2a. Overall, the reaction is

$$H_2 + Cl_2 \rightarrow 2HCl. \quad (1)$$

One of the first observations made of this reaction is the dependence of its rate on the amount of light present. In the dark, it proceeds relatively slowly. However, in light the two gases combine quite rapidly, or even explosively. Therefore, it has been suggested that the reaction takes place according to the following mechanism: at the onset, a priming reaction leads to free radical formation by photochemical means, or by thermal decomposition of chlorine molecules, or by some other cause.

In this case, the reaction is begun photochemically when light strikes the molecules, supplying energy for dissociation to free radicals. Thus:

$$h\nu\text{light} \rightarrow Cl\cdot + Cl\cdot. \quad (2)$$

This is referred to as the initiation reaction. The chlorine free radicals will subsequently react with hydrogen molecule:

$$Cl\cdot + H_2 \rightarrow HCl + H\cdot. \quad (3)$$

In turn, the hydrogen free radical reacts with a chlorine molecule, regenerating another Cl· radical:

$$H\cdot + Cl_2 \rightarrow HCl + Cl\cdot. \quad (4)$$

From this point, reactions (3) and (4) occur in alternate fashion to form the chain reaction. These reactions are said to be links of the chain, while the free radicals H· and Cl· are called active centers or agents of the chain reaction.

At some point in the reaction, destructive processes come into play. These are capable of "removing" the active centers from reactions (3) and (4), and they ensure that each priming reaction will be followed by a finite number of links. For example, the reformation of molecules from radicals can be destructive reactions:

$$Cl\cdot + Cl\cdot \rightarrow Cl_2 \quad (5)$$

$$H\cdot + H\cdot \rightarrow H_2. \quad (6)$$

In considering these destructive reactions, it must be noted that the reaction of two radicals is always accompanied by the production of considerable energy. If reactions (5) and (6) were to occur as written, the resulting molecules would possess far greater energy than normal. Consequently, these extremely unstable molecules would immediately dissociate.

In fact, if free radicals are to react and form stable molecules, the reaction must take place in the presence of some material that will absorb the liberated energy. This material could be the walls of the container in which the reaction occurs, or it could be other gaseous molecules. The process of terminating the chain reaction in this way is called quenching.

Where the initiation reaction is of photochemical nature (2), it has been found that every quantum of light absorbed leads to the formation of about $10^5$ molecules of HCl; this gives some idea as to the length of the chain reaction.

The initiation reaction can also be chemical in nature. For example, the reaction between hydrogen and chlorine can be initiated by the presence of sodium vapor in small quantities. In this instance, it is assumed that the initiation reaction proceeds according to the equation:

$$Na\cdot + Cl_2 \rightarrow NaCl + Cl\cdot.$$

The resultant chlorine radical then proceeds as in reactions (3) and (4). Chemical initiation has been studied with equipment such as that shown in Illustration 2b. This special reaction chamber is constructed so that hydrogen molecules are mixed with sodium and chlorine gases, with the reaction as shown above. Sodium chloride is deposited on the chamber walls while hydrogen chloride molecules are formed. It has been determined that for each molecule of sodium chloride—that is, for every Cl· radical formed—about $10^4$ molecules of hydrogen chloride are produced.

In a reaction identical to that of hydrogen and chlorine, hydrogen and bromine can undergo a chain reaction. The major difference is in terms of energies required and produced.

Illustration 2c represents the synthesis of phosgene, $COCl_2$, from carbon monoxide and chlorine. The qualitative reaction is:

$$CO + Cl_2 \rightarrow COCl_2.$$

This reaction is also based on the chain mechanism, and is initiated photochemically. In this case, two Cl· free radicals are the result, the links in the chain being:

$$Cl\cdot + CO \rightarrow COCl\cdot \quad (7)$$

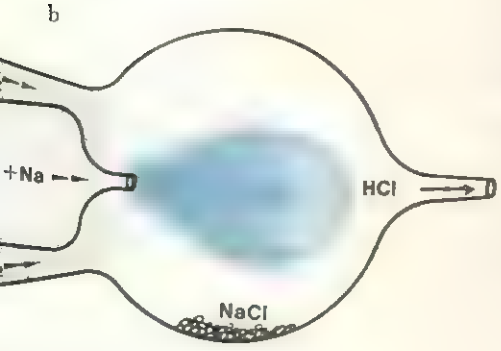
$$COCl\cdot + Cl_2 \rightarrow COCl_2 + Cl\cdot. \quad (8)$$

The destructive reaction here is:

$$COCl\cdot + Cl\cdot \rightarrow COCl_2. \quad (9)$$

Initiated by photochemical means, this reaction produces about $10^3$ molecules of phosgene for each quantum of light absorbed.

b

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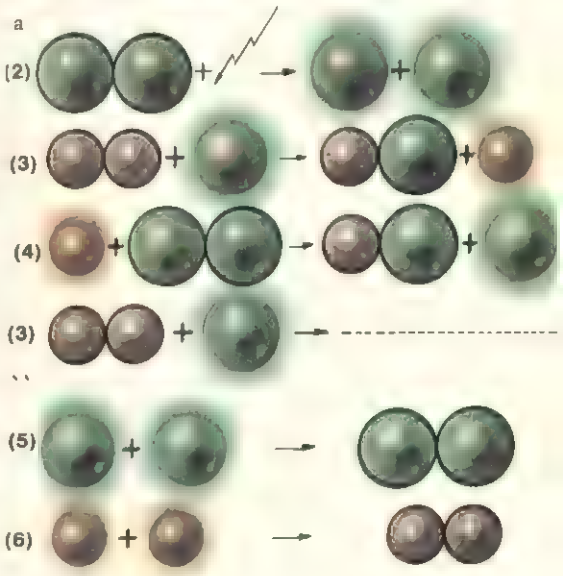





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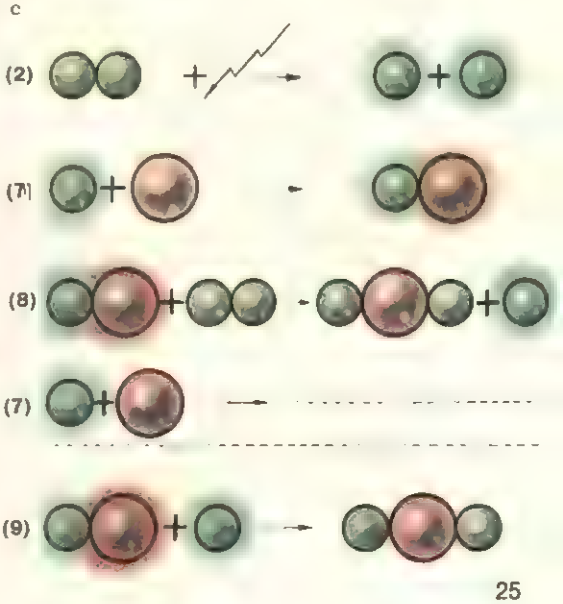


# FREE RADICAL CHAIN REACTIONS

## why hydrogen and oxygen explode

So-called simple chain reactions in which a given reactive species generates but one additional reactive particle were discussed in a previous article.

This article examines another group of chain reactions, the so-called branched-chain reactions. In these reactions each reactive particle generates two or more new ones. Chain reactions of this type often produce reactive particles so fast that the reaction may proceed with explosive speed, unless other reactions intervene to break the chain.

To illustrate how great a number of reactive particles can be formed by a single initiating particle, it is useful to recall the famous anecdote of the checkerboard and the grains of wheat.

A single grain of wheat is placed on the first square of the checkerboard, two on the second, four on the third, eight on the fourth, and so on. The number of grains from one square to the next is always doubled.

Since a checkerboard contains 64 squares, thousands of millions of tons of grain will be needed before the checkerboard is filled. To calculate how many grains will have to be placed on the 64 squares, start counting as follows:

$$1, 2, 4, 8, 16, 32, 64, 128$$

This is the number of grains on the first eight squares. The sequence continues for the remaining squares. This series of numbers can be expressed as:

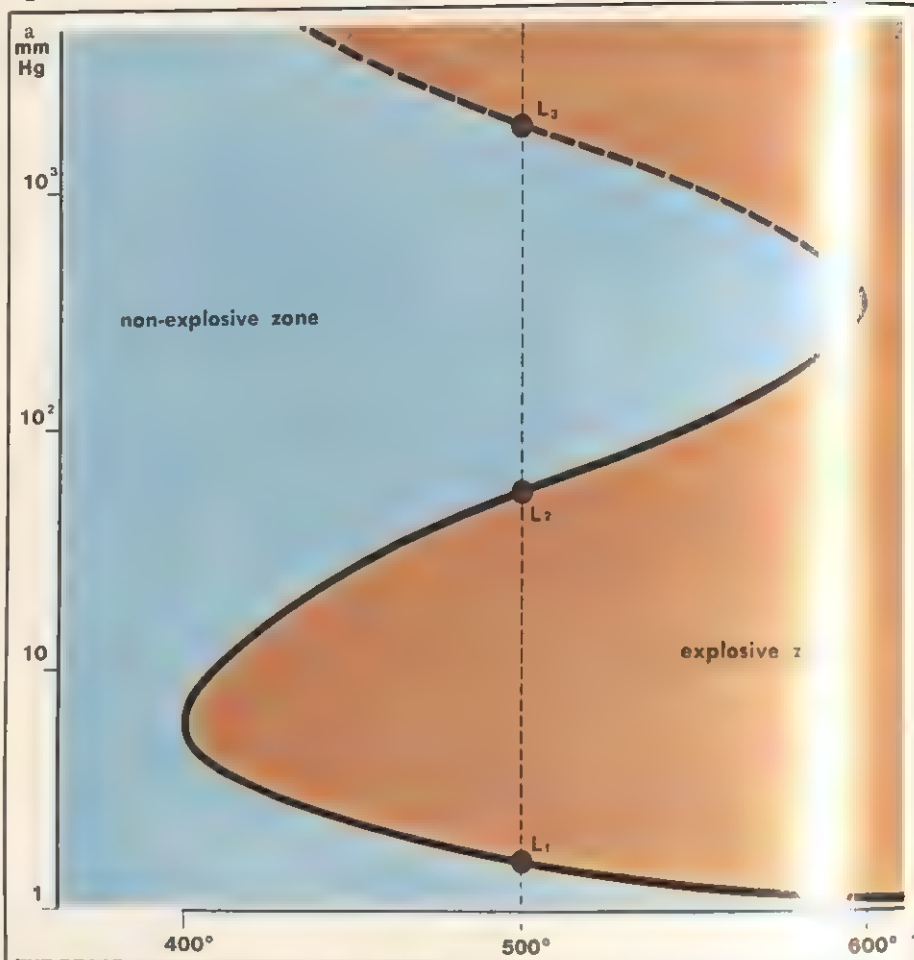
$$2^0, 2^1, 2^2, 2^3, 2^4, 2^5, 2^6, 2^7 \ldots\ldots 2^n.$$

This is a geometric progression. It can be shown that the sum of the first n terms of this progression is given by $(2^n - 1)$.

Thus $2^{64} - 1$ grains will be placed on the 64 squares of the checkerboard. This is approximately equal to $1.85 \times 10^{19}$ grains. Now, assuming that 1,000 grains of wheat weigh about 25 grams, the total weight of the grain turns out to be about $46.25 \times 10^{10}$ tons, or 46.25 times 10,000 million tons of grain.

A similar situation occurs in the case of branched-chain reactions. In fact, if any one reactive species always generates two reactive particles, these will generate four others, these in turn will generate eight, and so forth. Since each molecule will normally be involved in hundreds of collisions in a fraction of a second (a collision is needed to generate reactive particles of the reaction chamber, and others.

1




**THE REACTION OF HYDROGEN AND OXYGEN**—The reaction between hydrogen and oxygen takes place according to the overall formula

$$2H_2 + O_2 \rightarrow 2H_2O.$$

Study of this reaction, however, reveals a number of characteristics that cannot be explained in terms of simple chain reactions. Of particular importance is the fact that the speed of the reaction is dependent on pressure. For example, consider a mixture of hydrogen and oxygen at a temperature of 500° C (932° F). If the pressure is held below 1.5 mm of mercury, the reaction is rather slow. The speed of the reaction increases, however, as the pressure increases. When the pressure is slightly greater than 1.5 mm of mercury, the speed of reaction reaches explosive proportions. If the pressure is further increased to a point above 50 mm of mercury, the reaction once again takes place at a normal speed. The speed is measurable again and the reaction can be studied using normal laboratory equipment.

If the pressure is increased still further, another critical limit is reached at about 3,200 mm of mercury. At this point, the reaction once again becomes explosive. Therefore, three values of pressure define the zones within which the reaction is explosive. These limiting values depend on numerous experimental factors including temperature, the diameter of the reaction chamber, the nature of the inner sur-

Temperature dependence is illustrated by the graph shown in Illustration 1a. The orange area represents the conditions under which the reaction is explosive, and the points $L_1$, $L_2$, and $L_3$ represent the three limiting pressures at a temperature of 500° C.

In interpreting these phenomena, it has been suggested that the reaction may take place according to the mechanism described below.

The priming reaction could be

$$H_2 + O_2 \rightarrow 2OH\cdot$$

or

$$H_2 \rightarrow 2H\cdot$$

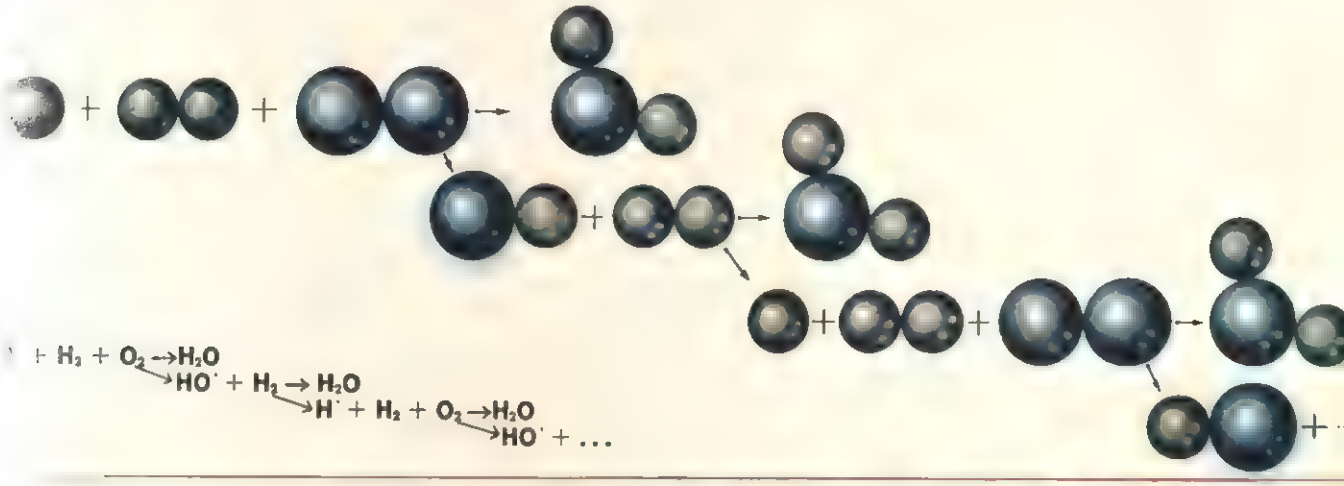
As usual, a chemical symbol with a single dot represents a free radical. Free radicals can react with other molecules in such a way that each radical gives rise to a single new radical. Under these conditions, the chain reaction will be a simple one; its steps are as follows:

$$H\cdot + O_2 + H_2 \rightarrow H_2O + OH\cdot$$
$$OH\cdot + H_2 \rightarrow H_2O + H\cdot$$

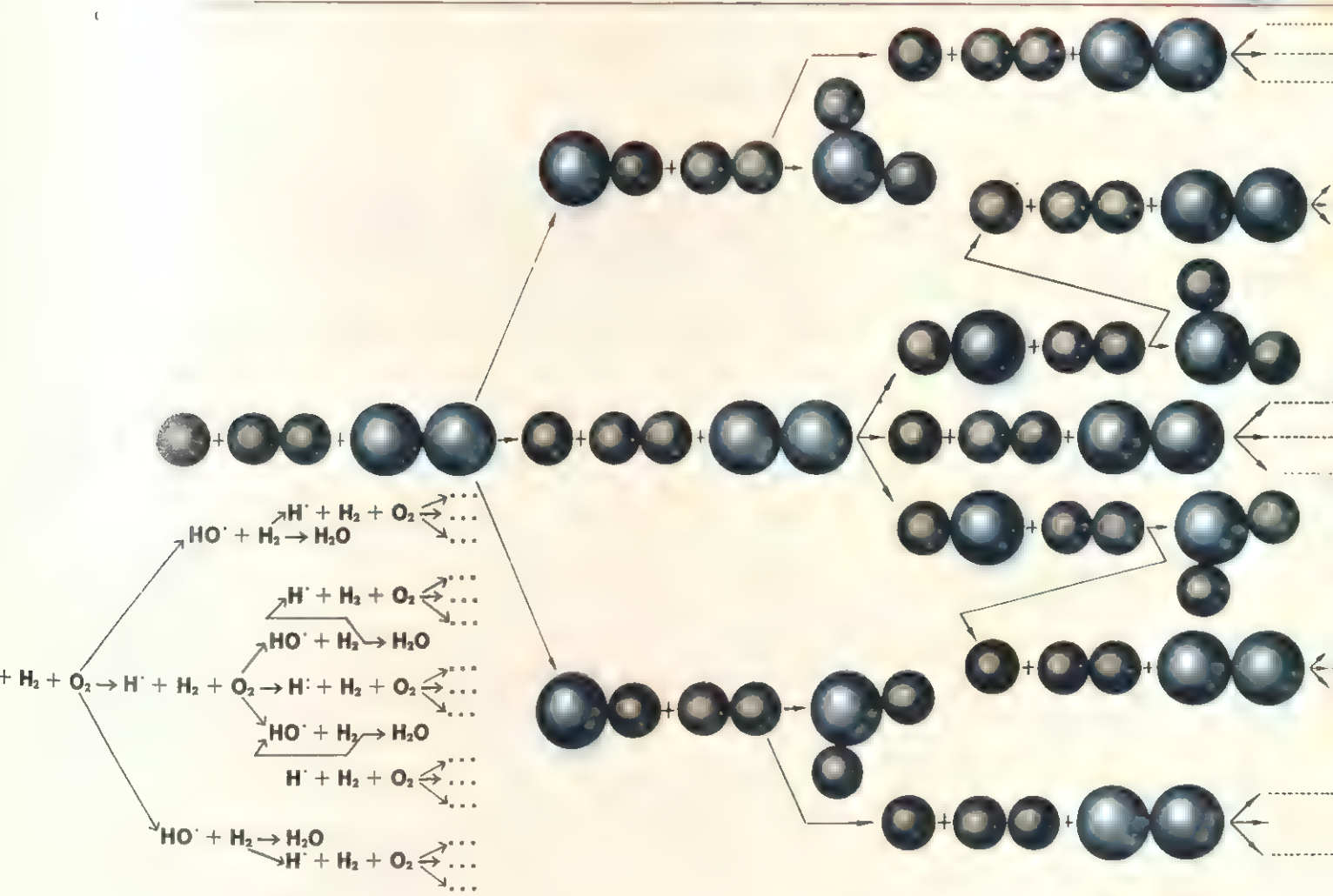
These reactions are schematically illustrated in Illustration 1b.

It is also possible for the initial reaction to be followed by others in which each free radical generates two or more additional free radicals. In this case the reaction is said to be a branched-chain reaction:

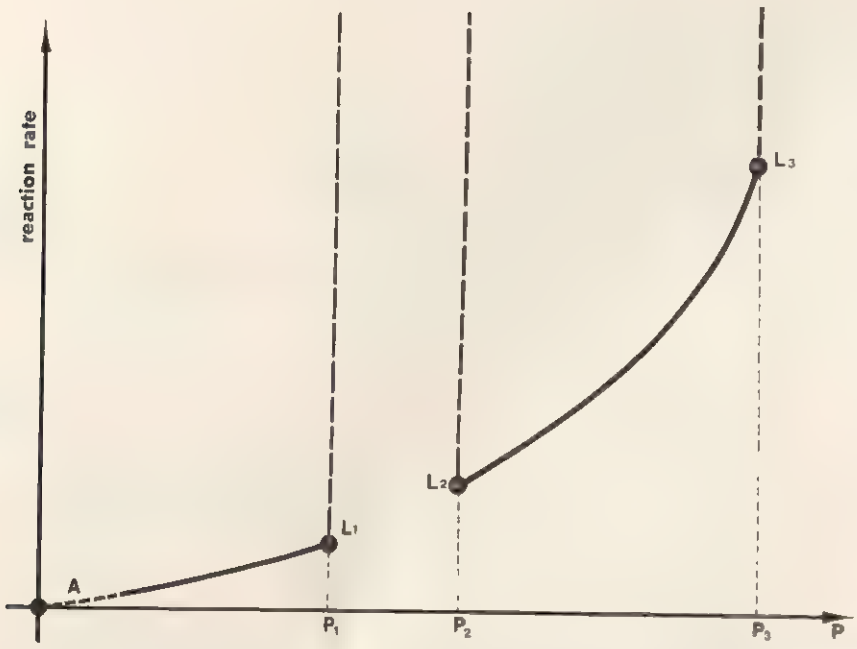
b


+ H₂ + O₂ →H₂O
HO˙ + H₂ → H₂O
H˙ + H₂ + O₂ →H₂O
HO˙ + ...

c


+ H₂ + O₂ → H˙ + H₂ + O₂ → H˙ + H₂ + O₂
HO˙ + H₂ → H₂O
H˙ + H₂ + O₂
HO˙ + H₂ → H₂O
H˙ + H₂ + O₂
HO˙ + H₂ → H₂O
H˙ + H₂ + O₂
HO˙ + H₂ → H₂O
H˙ + H₂ + O₂

d




$$H\cdot + O_2 \rightarrow OH\cdot + O\cdot \quad (1)$$

$$O\cdot + H_2 \rightarrow OH\cdot + H\cdot \quad (2)$$

$$H\cdot + O_2 + H_2 \rightarrow H\cdot + OH\cdot + OH\cdot \quad (3)$$

In this case the chain divides and branches because each of the new free radicals will initiate a new cycle of reactions (schematically represented in illustration 1c).

Such a reaction might be terminated, for example, by the following:

$$H\cdot + O_2 \rightarrow \cdot O_2H. \quad (4)$$

Contrary to appearances, this is a damping reaction because the $\cdot O_2H$ free radical will immediately destroy itself against the walls of the reaction chamber. That such damping reactions occur very readily against the walls of the reaction chamber is demonstrated by the introduction of glass wool. This always causes an increase in the number of damping reactions, and, consequently, a reduction in the speed of the overall reaction.

On the basis of reactions (1) and (4) above, the influence of pressure on the speed of the reaction can be explained as follows: The pressure (and consequently also concentration) of the gas is so low below the first limit $L_1$ that most of the free radicals formed during the initiating reactions reach the walls of the reaction chamber without becoming involved in any collisions with other molecules. These free radicals thus self-destruct on the walls and the chain reaction cannot continue. As a result, the speed of the reaction will be rather low. Increasing the pressure, however, also increases the number of molecules per unit volume; this will necessarily increase the probability that a free radical will collide with another molecule. When the various propagation or branching reactions are more numerous than damping reactions, the number of free radicals in the mixture increases at an extremely rapid rate and the reaction becomes explosive.

If the pressure continues to increase, damping reactions assume a greater importance; they then become so numerous at the second limit $L_2$ that the reaction ceases to be explosive.

Increasing the pressure still further moves the system to a third explosive limit $L_3$. This limit is very difficult to study experimentally because it occurs at very high pressures and because it is strongly influenced by the nature of the reaction chamber. It has not been possible to explain completely the physical reasons for this upper explosive range. It has been shown, however, that the explosive reaction in this range is no longer due to the extremely fast rate with which the chain reaction gathers momentum. The existence of this limit may be due to the fact that enormous numbers of molecules become activated in a very brief time.

The graph in illustration 1d represents the behavior of the hydrogen-oxygen mixture at a temperature of 500° C. This graph is obtained by plotting the reaction rate against the pressure (abscissa) at any arbitrarily chosen point. The speed of the reaction is finite along the curve $AL_1$.

The first explosive limit occurs at a pressure of 1.5 mm of mercury ($P_1$). The reaction is explosive in the interval $L_1$-$L_2$; here the speed of reaction is extremely great. The point $L_2$, corresponding to a pressure $P_2$ of 50 mm of mercury, is the second explosive limit. The speed of the reaction is once again measurable along the curve $L_2L_3$, but at the third explosive limit $L_3$ ($P_3$ = 3,200 mm of mercury) the reaction will again assume explosive proportions.

ticles), the reaction would u ubtedly become explosive if all the ollisions were productive and if dan g reactions were not equally num

Of all the branched-cha eactions known, this article will des in some detail the reaction between ous hydrogen and gaseous oxygen. reaction takes place according to general formula:

$$2H_2 + O_2 \rightarrow 2H_2($$

There is some evidence to ate that chain reactions take place o walls of the reaction chamber. In fa a stream of oxygen is allowed to mi ow pressure with a stream of hydro n a very large container, no explosio curs. An explosion will occur, ho if the gases are allowed to mix un the same conditions in a much sma ontainer.

For this reason, it is tho that the free radicals (reactive spe that initiate the chain reaction form he walls of the container. They ma form on the surface of any other l (a glass rod, for example) inside th tainer at the point where the two st s of gas come into contact. Under ent conditions, of course, different ting reactions will occur. This ph enon has also been observed in other tions.

In addition to this reactio number of others proceed in a mann imilar to the chain reaction between eous hydrogen and oxygen. These reactions, because of their considerable theoretical interest, have been extensively studied. Included in this group are the oxidation of phosphine:

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O;$$

the oxidation of carbon disulfide:

$$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2;$$

and the oxidation of carbon monoxide:

$$2CO + O_2 \rightarrow 2CO_2.$$

Finally, there are the very important chain reactions that occur in atomic bombs and in atomic piles. These reactions, however, involve nuclear processes and cannot be regarded as chemical reactions.

# PHOTOCHEMICAL REACTIONS

## light energy and chemical reactions

Some chemical reactions are initiated or accelerated if the reacting substances are exposed to appropriate light radiations. Such reactions are called photochemical reactions. Reactions not influenced by light are known as dark or thermal reactions. The term thermal reaction refers to the fact that the speed of a dark reaction depends in large measure on the temperature of the reacting system.

Many photochemical reactions are of biological interest. One of the most important of these reactions is photosynthesis. In the presence of chlorophyll, plants are capable of utilizing light energy in the production of carbohydrates and oxygen from raw materials that consist of carbon dioxide, $CO_2$, and water, $H_2O$. Man and many other animals perceive light by virtue of a photochemical reaction. The eye contains rhodopsin, a compound consisting of vitamin A (or retinol) combined with a protein. Light splits rhodopsin into protein and retinene (vitamin A dehydrogenated by means of an aldehyde). The brain then perceives the effect of the light in terms of the concentration of retinene. With the help of certain enzymes, the rhodopsin then reforms in the dark.

Other photochemical reactions are important in photography. Black-and-white photographs, for example, depend on light-initiated decomposition of silver halides. The same reaction is used in color photography to produce another reaction that deposits a colored pigment in the immediate area of the decomposed silver halide molecule. Photochemical reactions seem to be an essential part of modern civilization.

Before explaining the principles of photochemical reactions, it is necessary to make a brief analysis of the nature of light (electromagnetic) radiation.

### LIGHT RADIATIONS

The term radiation refers to periodic variations of an electromagnetic field in space. These variations can cover a vast range of wavelengths. According to the quantum theory, electromagnetic radiation may be regarded as consisting of particles known as photons or quanta. The energy of each quantum is given by $\epsilon = h\nu$.

In this equation $h$ represents Planck's constant ($6.62 \times 10^{-27}$ erg/sec), while $\nu$ represents the frequency of oscillation of the radiation (that is, the number of oscillations, or cycles, that occur in unit time—one second). The frequency $\nu$ is related to the wavelength $\lambda$ of the radiation by the expression $\nu = c/\lambda$. The term $c$ is the speed of electromagnetic radiation. Provided that both the wavelength of the radiation and the speed of light $c$ ($3 \times 10^{10}$ cm/sec) are known, these two equations permit calculation of the energy of a single quantum, or photon of light.

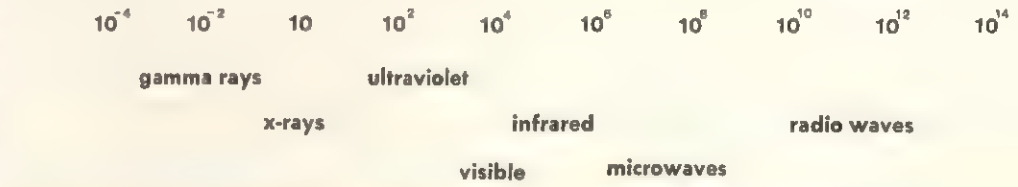
Carrying out this calculation not for the energy of a single photon ($\epsilon$), but rather for the energy $E$ of $N$ photons ($N$ is Avogadro's constant: $6.023 \times 10^{23}$), the result is

$$E = \frac{2.86 \times 10^{8}}{\lambda} \text{ calories/mole},$$

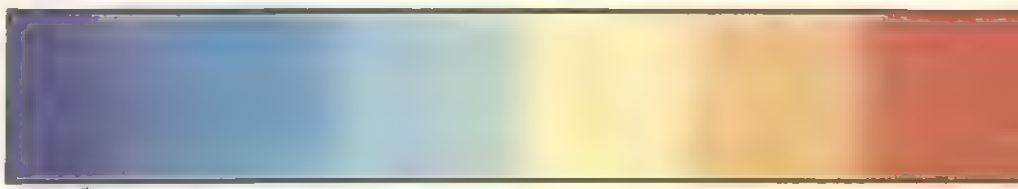
where the wavelength $\lambda$ is expressed in Angstroms ($1\,\text{Å} = 10^{-8}$ cm). This equation demonstrates that the energy of electromagnetic radiation is inversely propor-

1

a



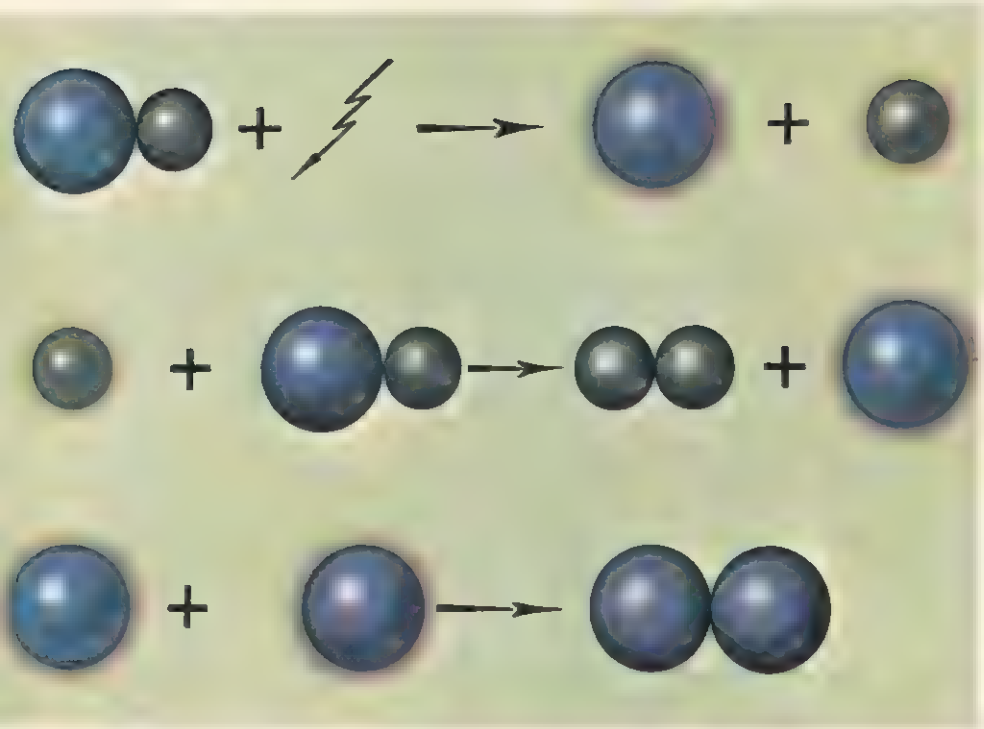

b




c

| RADIATION | WAVELENGTH, in Å | ENERGY OF RADIATION in kcal/mole |
|---|---|---|
| gamma rays | 0.1 | about 3,000,000 |
| x-rays | 1 | about 300,000 |
| ultraviolet | 1,000 | about 300 |
| ultraviolet | 4,000 | about 70 |
| visible | 5,000 | about 60 |
| visible | 6,500 | about 45 |
| infrared | 10,000 | about 30 |
| infrared | 200,000 | about 1.5 |

**THE ELECTROMAGNETIC SPECTRUM**—Illustration 1a shows how electromagnetic radiation varies gradually from gamma rays to x-rays, from ultraviolet radiation to visible light and the far infrared; beyond these the spectrum includes microwaves and radio waves. The visible portion of the spectrum is shown in illustration 1b. Lastly, the table (illustration 1c) shows the amount of energy associated with radiation of different wavelengths. The energy values shown in this table were calculated by means of the expression $E = 2.86 \times 10^{8}/\lambda$.



**THE DISSOCIATION OF HYDRIODIC ACID**—A very simple example of a photochemical reaction is the dissociation of hydriodic acid. The photochemical efficiency $R$ of this reaction has been shown experimentally to be equal to 2.

This reaction has been studied at various visible and ultraviolet wavelengths. The primary photochemical reaction $HI + h\nu \rightarrow H\cdot + I\cdot$ may be followed by

$$H\cdot + HI \rightarrow H_2 + I\cdot \quad \text{(a)}$$
$$H\cdot + H\cdot \rightarrow H_2 \quad \text{(b)}$$
$$I\cdot + I\cdot \rightarrow I_2 \quad \text{(c)}$$
$$I\cdot + HI \rightarrow I_2 + H\cdot \quad \text{(d)}$$
$$H\cdot + I\cdot \rightarrow HI \quad \text{(e)}$$
$$H\cdot + I_2 \rightarrow HI + I\cdot \quad \text{(f)}$$

Reactions (b) and (e) are so highly exothermic that the heat evolved causes the molecules to dissociate as soon as they have been formed. Reaction (d) is endothermic and requires a very high activation energy in order to occur. Reaction (f) is very unlikely due to the low concentration of $I_2$. The most probable reactions are therefore (a) and (c), both of which are illustrated above. Combining the initial reaction with these two reactions, the result is $2HI + h\nu \rightarrow H_2 + I_2$. This mechanism explains the photochemical efficiency of 2 for the reaction.

tional to its wavelength. The smaller the wavelength $\lambda$, the greater the energy $E$.

## THE LAWS THAT GOVERN PHOTOCHEMICAL REACTIONS

The first law of photochemistry states that radiation must be absorbed by a reactant molecule in order for a photochemical reaction to take place. This law, which is essentially qualitative, is intuitively understandable.

Einstein investigated the quantitative aspect of photochemical reactions in 1912. He derived the second law of photochemistry, the so-called law of equivalence. This law states that each photon absorbed by a reaction system activates one and only one molecule within the system. This does not necessarily mean that each activated molecule gives rise to a chemical reaction in the true sense of the word. There may also be any number of secondary effects. For this reason a new concept—the photochemical or quantum efficiency $R$ of a given reaction—is necessary. For any given period of time, the quantum efficiency $R$ is defined as the ratio of the number of molecules that have reacted to the number of photons that have been absorbed:

$$R = \frac{\text{number of molecules that have reacted}}{\text{number of photons absorbed}}.$$

$R$ obviously equals 1 if primary photochemical molecular activation is followed by chemical reaction with no secondary effects whatsoever. An example of a reaction with an efficiency $R$ very close to 1 is the photochemical reaction of monochloroacetic acid in aqueous solution:

$$CH_2ClCOOH + H_2O \xrightarrow{\text{photon}} CH_2OHCOOH + HCl.$$

Photons having a wavelength of 2,537 Å will initiate this reaction. Such photons can be obtained from excitation of mercury vapor in a suitable lamp.

The quantum efficiency $R$ of a reaction will be greater than 1 when primary photochemical activation is followed by secondary dark reactions. Such reactions increase the value of the numerator in the efficiency equation. A chain reaction in which the primary reaction is caused by absorption of a photon is an excellent example of a photochemical reaction with high efficiency.

Reactions also occur for which the photochemical efficiency $R$ is less than 1. Several reasons may underlie such an occurrence. The most common occurrence is loss of energy when a photochemically excited molecule collides with another molecule before it has a chance to react. This dissipates a portion of the photochemical activation energy in the form of translational energy. The result is an increase in the temperature of the system. A variation occurs when the second molecule becomes excited and enters a chemical reaction. This is referred to as excitation by sensitization.

In another instance, the excited molecule may reradiate a portion of the absorbed energy. This is called fluorescence. When such an excited molecule reradiates energy, the wavelength of the reemitted light will generally be longer than that of the originally absorbed light, because less energy is reradiated, the difference being lost in vibration of energy, primarily.

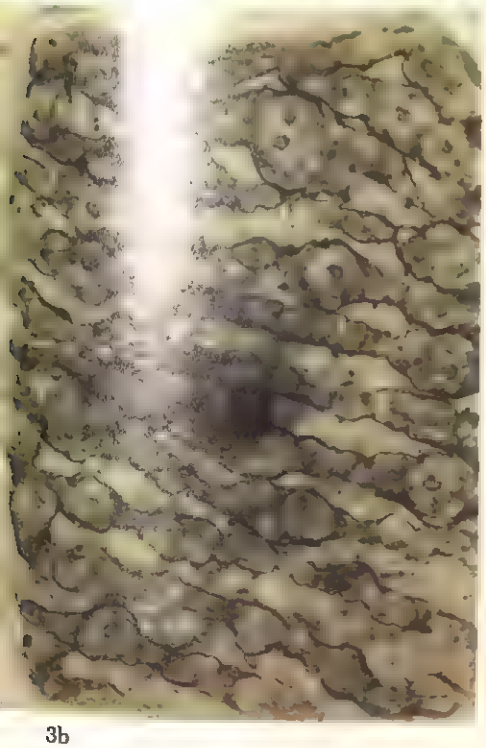
Phosphorescence is a phenomenon somewhat akin to fluorescence. The term phosphorescence stems from the occurrence of a similar phenomenon in phosphorus. In phosphorescence, the emission of radiation persists for a longer period of time; it continues even after the action of the exciting radiation has ceased. Many substances that are fluorescent in aqueous solutions become phosphorescent when dispersed in a solid.

One example of a photochemical reaction with an efficiency less than 1 is the decomposition of oxalic acid in a solution sensitized by a uranium ion. This reaction, whose efficiency is 0.50 for a wavelength of absorbed energy of $\lambda = 4{,}350$ Å, has been extensively studied because its course can be followed easily by means of titration with potassium permanganate. The results of the titration are very easily reproduced. For this reason this reaction has been proposed as a method for determining the quantity of light emitted by light sources.

Experimental observations such as those discussed show that measurement of the photochemical efficiency $R$ of a reaction is of fundamental value.

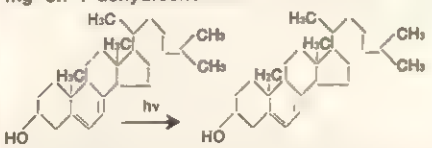
**PHOTOSYNTHESIS**—The synthesis of carbohydrates is essential for the continued existence of plants, which are autotrophic. In photosynthesis, the green pigment of chlorophyll absorbs radiant energy in the visible range of the spectrum, and then re-emits this energy. The re-emitted energy is the activation energy for the series of reactions that lead to the biosynthesis of carbohydrate. The exact nature of the initial photochemical reaction is not clearly understood. Observations carried out using radioactive isotopes, however, suggest that it is very likely the splitting of a water molecule. Indeed, the oxygen released during photosynthesis by the plant does not come from the absorbed carbon dioxide, but rather from the water. The illustrations show an enlarged portion of the surface of a leaf (illustration 3a) and a chloroplast (illustration 3b).

3a

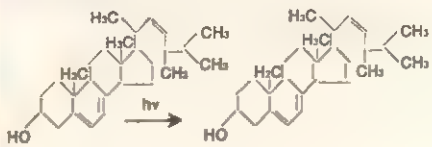


3b

An important large-scale application of photochemical reactions is the production of vitamin D, the anti-rickets factor. It had been known for many years that rickets regressed with intense exposure to sunlight. Then it was discovered that the anti-rickets factor (vitamin $D_3$) was produced by ultraviolet radiation acting on 7-dehydrocholesterol in the skin.




Synthetic vitamin D is produced by exposing ergosterol—obtained from yeast—to ultraviolet radiation.




4

**PHOTOCHEMISTRY AND PHOTOGRAPHY**—Photography is based on the photochemical reaction

$$AgBr \xrightarrow{h\nu} Ag\cdot + Br\cdot$$

When light strikes the emulsion of AgBr on sensitized paper, finely divided silver is produced. This silver is black. The photosensitive emulsion is more sensitive to blue and green light because these wavelengths have the highest energies within the visible spectrum. Red light, on the other hand, does not cause decomposition of the silver bromide in the emulsion.

The addition of special sensitizers to photographic emulsions produces orthochromatic and panchromatic films. The sensitivity of these films is similar to that of the human eye, and covers the entire visible spectrum.

# CHEMICAL EQUILIBRIA

## the law of mass action

Contrary to popular belief, a chemical reaction rarely continues until one of the reagents has been completely used up. More often than not, equilibrium is established before this point has been reached. A good example is the reaction of hydrogen and iodine:

$$H_2 + I_2 \rightarrow 2HI.$$

The product is hydrogen iodide. If the quantities of hydrogen and iodine are equimolecular, the reaction stops short of the completion point. Put another way, the quantity of hydrogen iodide reaches a maximum after a certain amount of time, depending on the conditions under which the reaction is carried out. The cause of this phenomenon is the fact that the reaction

$$H_2 + I_2 \rightarrow 2HI$$

is opposed by a second, exactly opposite reaction

$$2HI \rightarrow H_2 + I_2.$$

As the first reaction proceeds, the quantity of hydrogen iodide increases. At the same time, however, the reverse reaction takes place until the rate of the forward reaction is exactly equal to the rate of the reverse reaction. Under these conditions, a reaction is said to have reached equilibrium. This is written as follows:

$$H_2 + I_2 \rightleftarrows 2HI.$$

A chemical equilibrium of this type is not static, but rather dynamic (the number of HI molecules that form is exactly equal to the number of HI molecules that break up in a given period of time).

The system is called a homogeneous equilibrium when it consists of one phase (for example, the gas phase of the case described above), and a heterogeneous equilibrium when it consists of two or more phases. An example of a two-phase system is the thermal dissociation of calcium carbonate:

$$\underset{\text{(solid)}}{CaCO_3} \rightleftarrows \underset{\text{(solid)}}{CaO} + \underset{\text{(gas)}}{CO_2}.$$

Homogeneous equilibria consist of reactions between gases and reactions in solution. Heterogeneous equilibria account for the rest. For equilibrium to exist each of the reaction components must be at the same temperature and at the same external pressure.

Certain reactions take place quite slowly. In these instances it is convenient to regard the reaction as being in equilibrium, even though it is not. For example, a mixture of chlorine and hydrogen can be kept in storage, at room temperature and in the dark, for many days without any appreciable quantity of hydrogen chloride forming ($H_2 + Cl_2 \rightleftarrows 2HCl$). A system of this type is said to be in metastable equilibrium. If, however, the reaction is accelerated in some way (by using a catalyst, for example), the system will quickly reach a condition of real equilibrium. The term stable equilibrium is then applied.

### HOMOGENEOUS EQUILIBRIA

The study of chemical equilibria is of considerable importance. Many desirable reactions were made suitable for industrial processes only after a way had been discovered to manipulate their equilibria in favor of certain products.

Consider now the general equation for the equilibrium constant of a homogeneous system (already mentioned in the article on solubility):

$$aA + bB \underset{V_2}{\overset{V_1}{\rightleftarrows}} cC + dD.$$

Since the reaction rate, at constant temperature, is proportional to the concentration of each of the various reactants, the reaction rate from left to right may be reduced to the following type of equation:

$$V_1 = K_1 [A]^a \cdot [B]^b.$$

The quantities in square brackets stand for the concentrations of the reaction components at equilibrium. These concentrations can be expressed in terms of moles/liter, mole fraction (the ratio of the number of moles of a reactant at equilibrium to the total number of moles), or partial pressure (mole fraction multiplied by the total pressure).

The rate of the reverse process, on the other hand, is

$$V_2 = K_2 [C]^c \cdot [D]^d.$$

At equilibrium, the rates of the forward reaction and the reverse reaction must be equal. In symbols, $V_1 = V_2$. It follows that

$$K_1 [A]^a \cdot [B]^b = K_2 [C]^c \cdot [D]^d$$

and

$$K_c = \frac{K_1}{K_2} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}.$$

$K_c$ is the equilibrium constant at a given temperature (the concentration of the products is conventionally shown in the numerator, whereas the concentration of the reactants is shown in the denominator).

This concept may now be applied to the reaction in which hydrogen iodide is formed from hydrogen and iodine:

$$H_2 + I_2 \rightleftarrows 2HI$$

In this case the equilibrium constant is given by the expression:

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}.$$

Since this is a system in the gaseous phase, the equilibrium constant can be expressed as $K_p$; that is, in terms of the partial pressures of the products and reactants. Each partial pressure is raised to a power equal to the reaction coefficient:

$$K_p = \frac{P^2_{HI}}{P_{H_2} \cdot P_{I_2}}$$

The equilibrium constant takes on different values in terms of how the concentrations are expressed.

This law, known as the law of mass action, applies to electrolytic dissociation as well as chemical equilibria. Consider the case of a weak acid, acetic acid. Since it is a weak acid, only a few molecules will be dissociated in aqueous solution. The equilibrium is:

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$

and the constant is:

$$K_c = \frac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]\,[H_2O]}.$$

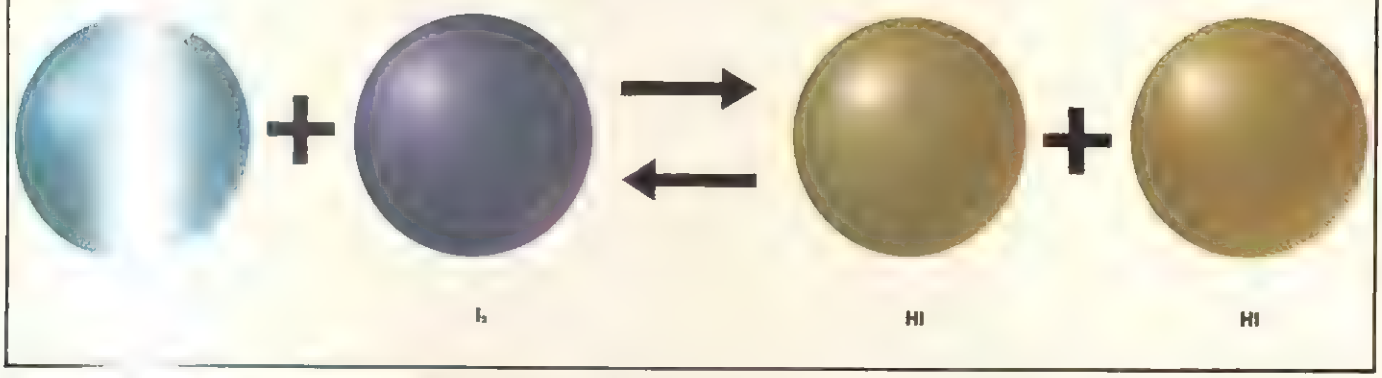
Since the concentration of $H_2O$ is virtually constant because of its presence in great excess, it can be included as part of $K_c$. The new constant, called the acidity constant, is therefore:

$$K_a = K_c \cdot [H_2O] = \frac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]}$$

The advantage of this constant is that it shows how strong an acid is. The higher its numerical value, the more dissociated (that is, the stronger) the acid. The following table lists typical constants, at 25° C (77° F), for a number of acids.

| | | |
|---|---|---|
| sulfurous acid | $HSO_3H$ | $1.7 \times 10^{-2}$ |
| acetic acid | $CH_3COOH$ | $1.8 \times 10^{-5}$ |
| carbonic acid | $HCO_3H$ | $4.3 \times 10^{-7}$ |
| hydrosulfuric acid | HSH | $9.1 \times 10^{-8}$ |
| hydrocyanic acid | HCN | $7.2 \times 10^{-10}$ |

1




**LE CHAT** **S PRINCIPLE**—Le Chatelier's principle hat if there is a variation in one of the rs causing a system to be at equilibrium quilibrium tends to shift in a direction unteracts the effect of the variation. ustration of this rule is the effect of pr variation at constant temperature. An i e in pressure favors reactions involving a ase in volume, whereas a decrease in ire favors reactions involving an increas olume.

Illustrat hows the formation of hydrogen iodid reaction does not produce a change in al volume (one volume of hydrogen pl of iodine yields two volumes of hydrog de); hence, the system is not affected b ure change.

Illustrat on the other hand, shows a reaction t os from two volumes of nitrogen diox to only one volume of nitrogen tet $N_2O_4$—a decrease in volume. Le r's principle predicts that an increase ssure will lead to an increase in the qu f nitrogen tetroxide.

The ma ical explanation of this phenomenon s follows: for the reaction $H_2 + I_2 \rightleftarrows$

$$K_c = \frac{[HI]^2}{[H_2]\ [I_2]}. \qquad (1)$$

If the concentrations in this equation are replaced with the partial pressures

$$P_{I_2}, P_{H_2}, P_{HI},$$

the result is

$$K_p = \frac{P^2_{HI}}{P_{H_2} \cdot P_{I_2}}. \qquad (2)$$

The total pressure of the system is equal to the sum of the partial pressures:

$$P_{tot} = P_{I_2} + P_{H_2} + P_{HI}.$$

Now, if the total pressure is multiplied by a value $x$ (2, for example, thus doubling the pressure) the partial pressure will also be multiplied by the same value:

$$x\,P_{tot} = x\,(P_{I_2} + P_{H_2} + P_{HI})$$

$$x\,P_{tot} = x\,P_{I_2} + x\,P_{H_2} + P_{HI}.$$

Substituting in equation (2):

$$K_p = \frac{x^2\,P^2_{HI}}{x\,P_{H_2} \cdot x\,P_{I_2}}.$$

This expression is simplified by dividing by $x^2$. The result is that the value of the constant $K_p$ remains unchanged.

In the second case: $2NO_2 \rightleftarrows N_2O_4$

$$K_p = \frac{P_{N_2O_4}}{P^2_{NO_2}}.$$

Multiplying by $x$:

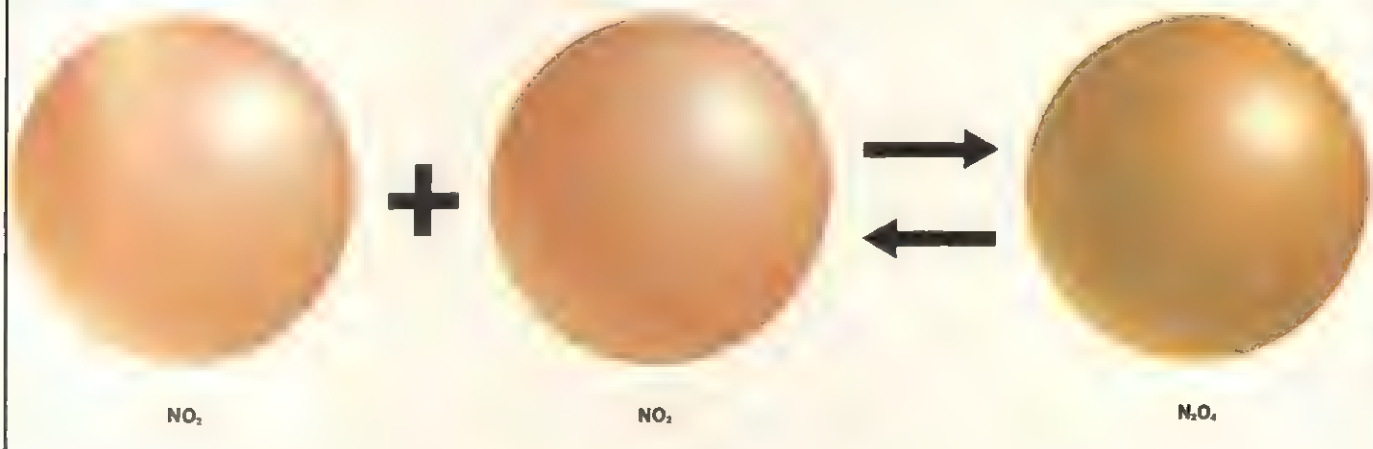
$$K_p = \frac{x\,P_{N_2O_4}}{x^2\,P^2_{NO_2}}.$$

Simplifying by dividing by $x$:

$$K_p = \frac{P_{N_2O}}{x\,P^2_{NO_2}}.$$

In this case the value of the denominator is increased by increasing the pressure. However, because the value of $K_p$ must remain constant, the value of the numerator will increase also.

2



## FACTORS CAUSING VARIATION IN AN EQUILIBRIUM SYSTEM

It is of great importance to know what happens to a system at equilibrium when it is affected by external factors. The fundamental rule governing equilibrium systems is Le Chatelier's principle (named after the French chemist Henry Louis Le Chatelier). This rule states that if the conditions of a system at equilibrium are altered, the equilibrium will shift in such a direction as to tend to restore the original conditions. Applied to pressure, this means that if a system at equilibrium and at constant temperature is compressed, the equilibrium will shift in the direction required to produce lower pressure and a consequent decrease in volume. An example will make this rule clearer. Consider again the reaction between hydrogen and iodine to produce hydrogen iodide. This reaction does not involve a change in the total volume (one volume of hydrogen and one of iodine produce two volumes of hydrogen iodide). The system is, therefore, unaffected by any variation in pressure.

It is a different story, however, with the dimerization reaction of nitrogen dioxide. In this reaction two molecules of $NO_2$ produce one of $N_2O_4$. Thus, the volume contracts by a factor of two:

$$\underset{\text{deep reddish brown}}{2NO_2} \rightleftarrows \underset{\text{colorless}}{N_2O_4}.$$

Adjustment of this equilibrium involves a variation in volume, but since the volume is directly dependent on pressure, the equilibrium will be affected by changes in pressure. If the pressure on a system containing a small amount of nitrogen tetroxide is increased, the equilibrium will shift to the right, dimerization will occur, and the color will gradually disappear (the monomer, $NO_2$, is colored; the dimer, $N_2O_4$, is colorless).

Le Chatelier's principle applies to temperature changes as follows. The equilibrium of a system at constant pressure reacts to a decrease in temperature by shifting in the direction in which heat is evolved. An example is the synthesis of ammonia according to the reaction:

$$3H_2 + N_2 \rightleftarrows 2NH_3 + 22{,}100 \text{ cal.}$$

The equilibrium constant for this reaction is:

$$K_c = \frac{[NH_3]^2}{[H_2]^3\,[N_2]}.$$

Since the reaction is exothermic, a drop in temperature will result in an equilibrium shift to the right—that is, toward an increase in the concentration of the ammonia and the evolution of heat. An increase in temperature has the opposite effect—a decrease in the concentration of the ammonia accompanied by the absorption of heat.

Another example is the synthesis of nitric oxide from nitrogen and oxygen according to the following reaction:

$$N_2 + O_2 \rightleftarrows 2NO - 43{,}200 \text{ cal}$$

where the equilibrium constant is:

$$K_c = \frac{[NO]^2}{[N_2]\,[O_2]}.$$

Here the reaction is endothermic. Since it is accompanied by the absorption of heat, a rise in temperature shifts the equilibrium to the right and results in an increase in the concentration of the NO. Conversely, a decrease in temperature shifts the equilibrium to the left and results in a decrease in the concentration of the nitric oxide.

In general, exothermic reactions are favored by low temperatures and endothermic reactions are favored by high temperatures. It should be noted, however, that practical experience provides examples of reaction situations that seem to contradict this rule.

To illustrate such a contradiction, consider again the synthesis of ammonia, $NH_3$, from nitrogen, $N_2$, and hydrogen, $H_2$. This is a most important industrial process because it uses atmospheric nitrogen. This reaction is exothermic and is accompanied by a decrease in volume (4 volumes of reactants yield 2 volumes of products). Thus, the reaction should be favored by low temperatures and high pressures. The fact is, however, that industrial processes for $NH_3$ production involving high pressures also involve temperatures of 400 to 500° C (752 to 932° F). The explanation is that while the reaction equilibrium constant, a thermodynamic factor, must be taken into account, so must kinetic factors. Kinetic factors refer to the rate at which a system reaches equilibrium. Although low temperatures, from a thermodynamic point of view, shift the equilibrium to the right, the same low temperatures greatly prolong the time required to reach equilibrium. This has the effect of reducing product output.

Recall, however, that an increase in temperature leads to an increase in reaction speed regardless of whether the reaction is endothermic or exothermic. Thus, a compromise is reached in practice.

The thermodynamic requirements of a reaction are balanced against an acceptable reaction rate; hence, the use of high temperatures.

Consider once again the equilibrium between iodine, hydrogen, and hydrogen iodide:

$$H_2 + I_2 \rightleftarrows 2HI.$$

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

If the hydrogen concentration is increased, the denominator of the equilibrium constant equation increases. It would seem that a corresponding decrease in the value of $K_c$ would occur. $K_c$, however, is a constant; hence, the actual result is an increase in the concentration of the hydrogen iodide. In other words, the system adjusts its equilibrium to the addition of hydrogen by forming more hydrogen iodide and maintaining the constant at its original value.

Another important topic is the effect of catalysts on systems at equilibrium. A system at equilibrium is not altered by the addition of a catalyst. A catalysts do is to lower the activation energy of the reaction (whether it is a forward or a reverse reaction). They thus increase the rate at which equilibrium is reached. What a catalyst cannot do is change the value of the equilibrium constant. In other words, the only effect of adding a catalyst is to stimulate the system to pass from metastable equilibrium to stable equilibrium. The catalyst cannot, however, cause a shift of the point of equilibrium itself.

## HETEROGENEOUS EQUILIBRIA

Heterogeneous systems, as mentioned, are those that involve more than one physical phase. Two very important principles apply to heterogeneous equilibria:

1. The activity of a substance has the same value in each phase of the system in which the substance is a component. In the water, ice, water-vapor system, for example, the activity of the water is the same in all three phases.
2. The activity of a substance in the liquid or pure crystalline phase is constant at constant temperature. Hence, the equilibrium constant may be expressed without including the substances that constitute these phases. For example, consider the equilibrium between calcium carbonate, calcium oxide, and carbon dioxide,

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

which is characterized by two solid components and one gaseous component. The equilibrium constant expressed in terms of partial pressures is:

$$K_p = \frac{P_{CaO} \cdot P_{CO_2}}{P_{CaCO_3}}$$

3a

3b

3c

**INFLUENCE OF CONCENTRATION ON AN EQUILIBRIUM SYSTEM** — Treating sodium chloride with a solution of sulfuric acid yields hydrochloric acid, as seen in the top portion of the flask in illustration 3a:

$$NaCl + H_2SO_4 \rightleftarrows HCl\uparrow + NaHSO_4.$$

At a given temperature an equilibrium is set up between the components of the system. This equilibrium is characterized by well-defined concentrations of the reactants and the products. Illustration 3a shows a certain amount of sodium chloride remaining in the bottom of the flask.

When the stopper is removed (illustration 3b), dense fumes of hydrogen chloride are produced until the sodium chloride has vanished completely (illustration 3c). By removing the hydrochloric acid from the equilibrium system, it is made to shift in the direction of producing more acid. In mathematical terms, a decrease in the numerator of the equilibrium constant equation is balanced by a similar decrease in the denominator:

$$K_c = \frac{[HCl][NaHSO_4]}{[NaCl][H_2SO_4]}.$$

The system counteracts the removal of hydrochloric acid by shifting the reaction to the right, thus using up the sodium chloride and the sulfuric acid.

The sodium chloride and the sulfuric acid react to produce the quantity of HCl required to reach equilibrium, but equilibrium is never attained because the acid continues to escape from the flask.

---

where $P_{CaO}$ and $P_{CaCO_3}$ represent the partial pressures of the calcium oxide and the calcium carbonate. These partial pressures, however, are constant and independent of the quantities of solid present. For this reason they may be included in the value of the equilibrium constant. The result is a new constant, $K'_p$

$$K_p = \text{constant} \cdot P_{CO_2};$$

therefore,

$$K'_p = P_{CO_2}.$$

This means that once the temperature has been established, the pressure of the carbon dioxide at equilibrium with the other two components is also constant. The same conditions hold for the equilibrium between carbon, carbon dioxide, and carbon monoxide (an important equilibrium, one of the factors that determine the temperature inside iron blast furnaces). This system consists of one solid component (carbon) and two gaseous components (carbon monoxide and carbon dioxide):

$$C + CO_2 \rightleftarrows 2CO.$$

Once again the equilibrium constant has a simplified form:

$$K_p = \frac{P^2_{CO}}{P_{CO_2}}.$$

## SOLUTION EQUILIBRIA—THE SOLUBILITY PRODUCT

A special case of solution equilibria occurs when the reaction being considered involves a component that is only slightly soluble. Such a situation exists for the equilibrium between silver chloride and the dissociated ions:

$$\underline{AgCl} \rightleftarrows Ag^+ + Cl^-.$$

Here the solid line under the silver chloride indicates it to be a precipitate; that is, it is rather insoluble in aqueous solutions. The equilibrium constant for this reaction is:

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}.$$

Because AgCl is only slightly soluble, the solution will be saturated with this substance, thereby making its concentration a constant. If this constant is combined with the equilibrium constant, a new constant is formed.

$$K_{sp} = K_c \times K_{AgCl} = [Ag^+][Cl^-].$$

This new constant, called the solubility product constant or simply the solubility product, is seen to depend only on the concentration of silver and chloride ions. Therefore, if the concentration of either of these ions is known, the concentration of the other can be calculated from the solubility product relationship. In addition, the solubility product can be used to predict the formation of a precipitate from a solution containing ions of known concentration. For example, the solubility product of AgCl is $K_{sp} = 1.56 \times 10^{-10}$ at 25° C (77° F). Because the dissociation of a single molecule of AgCl produces one $Ag^+$ ion and one $Cl^-$ ion, the concentration of these ions is the same if they all arise from AgCl dissociation.

Solubility product constants also enter into laboratory use.

# OXIDATION | the process that makes life possible

The world is full of examples of oxidation reactions; the flames gushing from the stacks of an oil refinery and the warm, life-giving flames of an open fire are both the result of oxidation. Another example is the physiology of breathing, the act performed mechanically and involuntarily throughout a lifetime.

The subject of oxidation has received the attention of scientists since earliest times. Many theories of oxidation, some

1

**FLAMES GUSHING FROM OIL REFINERY STACKS** — Exhaust gases ignite on contact with the air and undergo oxidation.

laborious, some merely childish, were put forward before the facts were finally assembled into a coherent and satisfactory explanation. The most famous of these early theories is undoubtedly the "phlogiston" theory, which until 1700 was universally accepted. Ancient scholars had observed that if a metal is heated in the presence of air, it loses its characteristic luster; after a time, its surface layer acquires an opaque, earthy appearance. It was deduced from this that metals were each composed of a different substance, and of something else that gave them their special luster, or their conductivity, or in general their characteristic properties. This something else was called phlogiston. When the metal was heated, it lost this extremely light and flammable "spirit," which was dispersed in the air, leaving behind only the basic substance, now opaque and lacking all of its natural properties.

But the ancients did not stop at this point. They also used the theory to explain other phenomena. They noticed, for example, that when certain opaque substances produced by combustion were heated with carbon, their former brightness returned. Why was this? The explanation offered was that carbon, being very rich in phlogiston, was generous enough to donate a little of it to any substance with which it came into contact. Observing that air contributed toward the transformation of lustrous metal into opaque substances, they concluded that air contained an element that absorbed phlogiston greedily whenever it got the chance. Since it was also observed that the transformation stopped at a certain point, it was deduced that the process stopped when the air reached a saturation point.

On the other hand, it did not escape the notice of these early scientists that the weight of the metal underwent a change during the transformation process. To be precise, it was noted that the substance remaining after combustion weighed more than the original metal. This obviously involved a gain, not a loss of something, light and immaterial as it might be. In chemical terminology, the process involved synthesis, not decomposition. This contradiction, however, was explained by the now-preposterous assumption that phlogiston possessed a negative weight. As is known today, the ancients were more concerned with quality than with quantity.

Toward the end of the eighteenth century, however, the space of just a few years saw a series of startling discoveries. In 1774, the English chemist Joseph

**RUST**—A piece of iron exposed to damp air soon becomes covered with a crusty layer of basic iron(III) carbonate. This process, which may continue indefinitely, involves conversion of the iron from an oxidation state of zero (the elementary state) to an oxidation state of 3+ (the compound). In other words, the iron is oxidized.

3

2

**BRAZIER**—Burning charcoal produces carbon dioxide $CO_2$, carbon monoxide CO, and other gases.

Priestley discovered and prepared oxygen. In 1777, the Swedish chemist C. W. Scheele also prepared it, working independently, and recognized it as a constituent of air. And in 1781 the French chemist Antoine Lavoisier established oxygen as the element involved in the processes of combustion and breathing.

What exactly is oxidation? In its common usage, the process can be defined as the combination of an element or substance with oxygen. Thus a metal such as magnesium combines with the oxygen of the air when heated and produces an oxide, which usually occurs as a powdery, opaque substance. The following experiment was made by Lavoisier. He placed some mercury in a retort with a long, curved neck. The end of the retort led under a bell in a basin containing more mercury (Illustration 6). Lavoisier then used a stove to heat the retort to

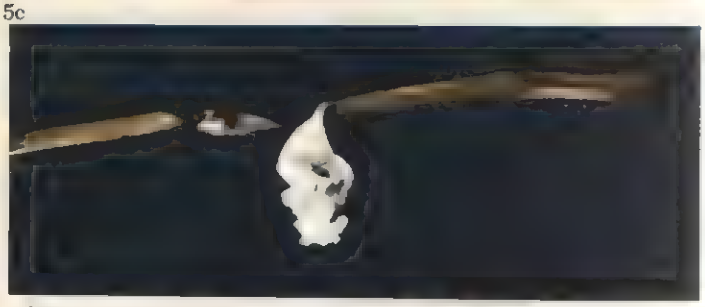
**STEEL INGOT DURING WEIGHING**—The oxidized layer on the surface of the incandescent mass tends to break away from the steel ingot because it has different physical properties.

**COMBUSTION OF MAGNESIUM**—Illustration 5a shows the characteristic metallic luster of magnesium shavings. When burned in air, magnesium produces a brilliant white flame (illustration 5b). The white powder remaining after combustion (illustration 5c) is magnesium oxide MgO. During oxidation magnesium goes from a valence of zero to a valence of +2.

5a

5b

5c



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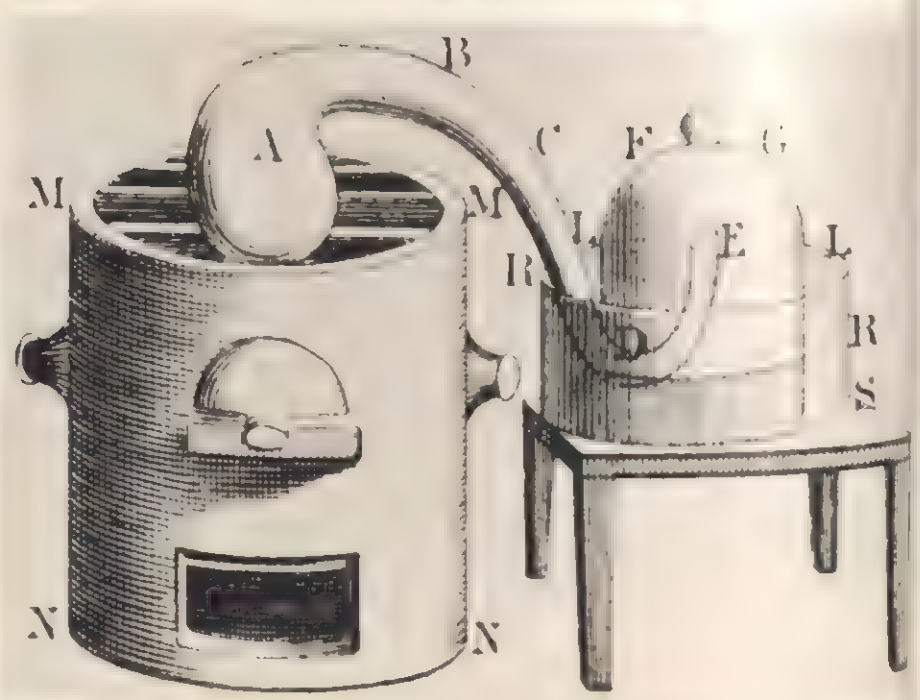


**LAVOISIER'S EXPERIMENT**—This contemporary print shows the equipment used by Antoine Lavoisier in 1781 for the famous experiment that identified combustion as oxidation and led to more acceptable theories of the composition of air.

7a

7b

**THE COMPOSITION OF AIR** — Illustration 7a shows that the candle continues to burn until it has used much of the oxygen in the air within the bell jar. Finally using up all the oxygen, the candle goes out (illustration 7b). Other gases, such as carbon dioxide and water vapor, have also been produced, but their volume is not great enough to occupy fully the space left by the oxygen. The water in the dish thus rises inside the bell to fill about 1/9 of the volume originally occupied by the air.

the boiling point of mercury. During this time a red powder formed in the retort, while the air trapped in the bell decreased by about 20 percent of its original volume. This was shown by the mercury level rising inside the bell to fill the space left vacant by the departing air. The retort, weighed before and after the experiment, showed an increase in weight. The conclusion was that the mercury had combined with the oxygen to produce the oxide—the red powder inside the retort. Other gases also developed during combustion, but the volume they occupied was much less than the volume occupied by the oxygen.

Here is another experiment, somewhat simpler than Lavoisier's, but equally revealing about the process of oxidation. (See Illustration 7.) A lighted candle is attached to a piece of cork, floated in a dish of water, and covered with a glass bell. The candle continues to burn until a portion of the air inside the bell has been used up, at which point the candle goes out. What has happened is that most of the oxygen inside the bell has been used up, leaving behind primarily nitrogen, the other basic component of air. Nitrogen does not support combustion. After enough time has elapsed for the temperature of the system to return to normal, the water in the dish will rise to fill the space previously occupied by the oxygen.

Oxidation thus means chemical combination of a substance with oxygen. The reaction for the mercury experiment is: $2Hg + O_2 \rightarrow 2HgO$. But this is not all. Oxidation also means the removal of hydrogen from a molecule, or the combination of an element with fluorine, chlorine, bromine, iodine, sulfur, and so on.

In chemical terminology, an element is oxidized when its atoms lose electrons. The substance causing the loss of electrons is known as the oxidant or oxidizing agent. The electron change for the mercury-oxygen reaction is as follows:

$$\begin{array}{ccccc} 0 & 0 & & +2 & -2 \\ Hg & + & O & \longrightarrow & HgO. \\ \downarrow & & \uparrow & & \\ 2e^- & & 2e^- & & \end{array}$$

The atoms of all elements in the elementary state—uncombined with other substances—have a zero charge, meaning that the number of electrons outside the nucleus is equal to the number of protons within the nucleus. Valence refers to the oxidation state or, to put it better, the electron state the atom assumes in combination. Mercury atoms in the elementary state have only two electrons in the outermost shell, while oxygen atoms have six. During reaction with oxygen the mercury atom loses these two electrons—it loses two negative charges—and becomes an ion with a charge of 2+. The oxygen atom, on the other hand, acquires the two negative charges and assumes a charge of 2−. These numbers are the valence numbers of the mercury and oxygen. Thus, two electrons are exchanged between one atom of mercury and one of oxygen. Since a molecule of oxygen consists of two atoms, however, two atoms of mercury are needed to supply the four electrons that are required for the overall reaction. The reaction thus becomes

**OXYGEN-HYDROGEN FLAME** — Oxygen and hydrogen combine to produce a flame that burns at about 2,300° C (about 4,172° F).

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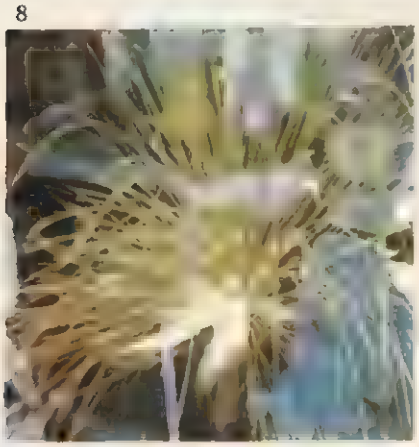

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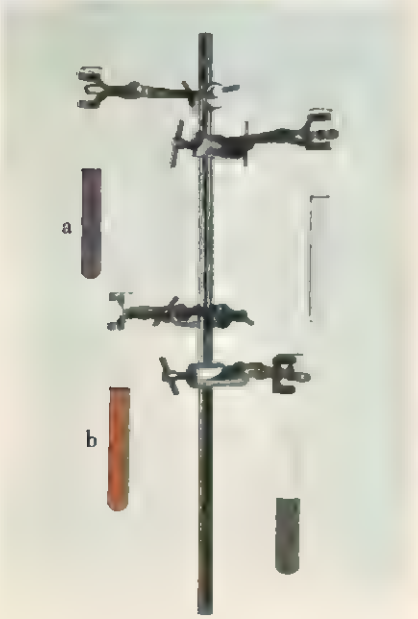


**OXIDATION-REDUCTION** — Color changes in the solutions show how the oxidation states of the ions change. In illustration 9a: $16HCl + 2KMnO_4 \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2$. Here the solution changes from dark violet—the characteristic color of potassium permanganate, where the ion involved is $MnO_4^-$—to pale pink—the characteristic color of manganese(II) chloride, where the ion is $Mn^{2+}$—at the end of the reaction. In illustration 9b: $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 \cdot Cr_2(SO_4)_3 + H_2O$. The orange solution (the dichromate ion $Cr_2O_7^{2-}$) turns green (the color of the $Cr^{3+}$ ion).

**FIREWORKS**—Combustion here is violent to the point of explosion. The oxidizing agent is first mixed with the gunpowder

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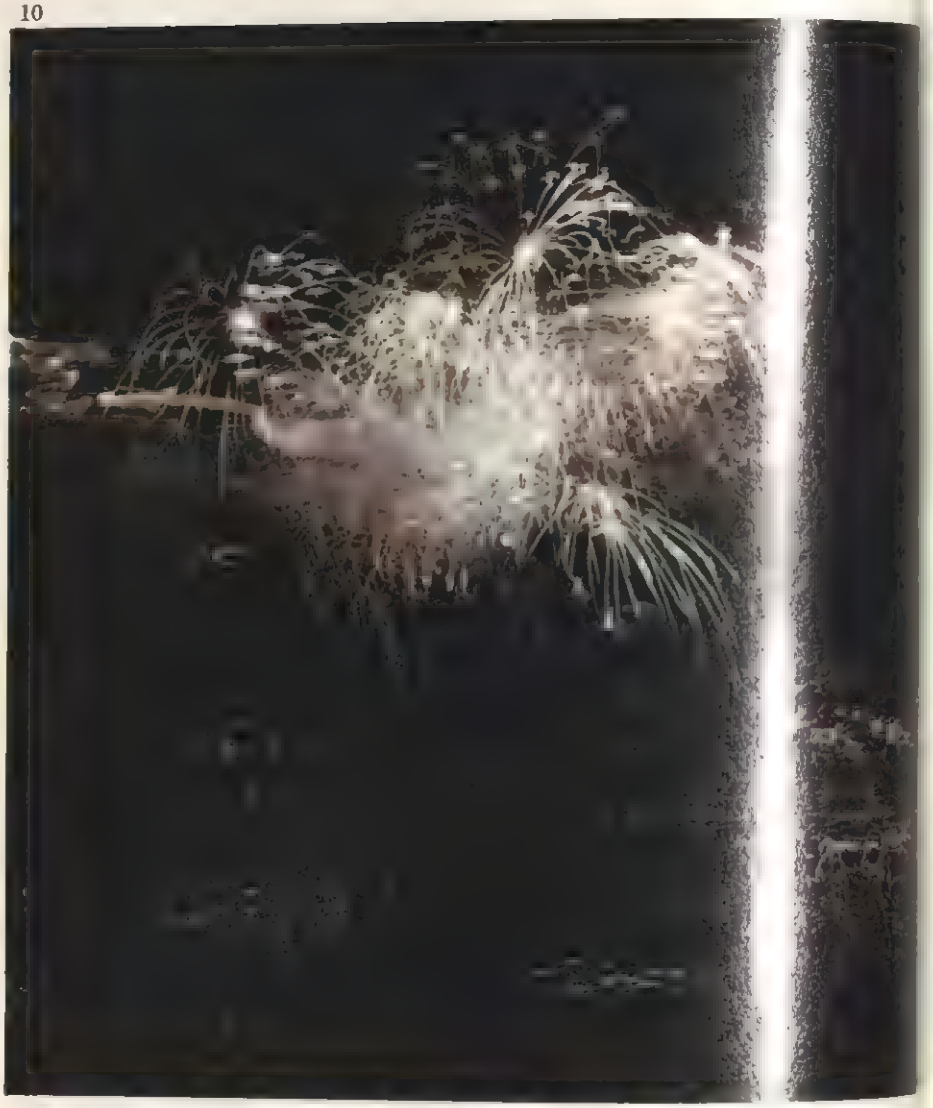


$$2Hg + O_2 \rightarrow 2HgO.$$

The result is two molecules of the oxide.

The reverse of the process of oxidation is known as reduction. Reduction is defined as a gain of electrons by a substance. In the example given above, the mercury lost two electrons and was therefore oxidized. The oxygen, which gained two electrons, was reduced. In every reaction in which a substance is oxidized, another substance is reduced. The reduced substance picks up the electrons lost by the oxidized substance. Every chemical oxidation is therefore simultaneously a reduction, and the term for the entire process is oxidation-reduction. Such reactions are sometimes called "redox" reactions.

Oxidants (substances that capture electrons) are numerous. Apart from oxygen and the halogens (chlorine, bromine, fluorine, iodine), already mentioned, there are hydrogen peroxide, potassium permanganate, potassium dichromate, potassium perchlorate, nitric acid, and many more. Reducing agents, which yield electrons, include hydrogen, carbon, alkali and alkaline-earth metals, sulfur dioxide, and ethyl alcohol. These substances and their reactions will be discussed later.

# OXIDATION-REDUCTION REACTIONS

## the balance sheet of masses and electrons

The reactions that take place with the transfer of electrons from one element, ion, or radical to another are called oxidation-reduction reactions.

An example of such a reaction involves sodium, an element of Group I. Sodium has a strong tendency to lose an electron from its outermost shell and assume a stable configuration (that of the noble gas neon), according to the reaction

$$Na \rightarrow Na^+ + e^-.$$

Chlorine (the second element in the group of the halogens) has seven electrons in its outermost orbit. Chlorine has a strong tendency to acquire an additional electron, attaining the stable configuration of the noble gas argon, in accordance with the equation

$$Cl + e^- \rightarrow Cl^-.$$

If some metallic sodium is placed in the presence of chlorine, the following reaction takes place:

$$Na + \tfrac{1}{2}Cl_2 \rightarrow NaCl,$$

in which the sodium has ceded one of its electrons to the chlorine and a bond has been established between the chlorine and the sodium.

| Variation in the number of electrons | Variation in the oxidation number | Terminology |
|---|---|---|
| loss of electrons | increases | oxidation |
| acquisition of electrons | diminishes | reduction |
| acquires electrons | diminishes | oxidizing agent |
| supplies electrons | increases | reducing agent |
| loses electrons | increases | oxidized substance |
| acquires electrons | diminishes | reduced substance |

This and analogous reactions that take place with the surrender (or acquisition) of electrons are called oxidation-reduction reactions. More precisely, the name of oxidation is applied to processes in which an element or an ion loses electrons, whereas reduction indicates processes in which an element or an ion gains electrons. The term oxidation was originally applied exclusively to those reactions in which a compound or an element combined with oxygen; only at a later stage did the term acquire its present, more general meaning.

When a compound loses a certain number of electrons (that is, when it is oxidized), the environment in which the reaction takes place must necessarily contain some other compound that acquires these electrons (this other compound is reduced).

The processes of oxidation and reduction are always so coupled; the oxidation of a substance (that loses electrons) causes the reduction of some other substance (that acquires the electrons lost by the first substance).

In the simple case previously described, for example, the sodium has ceded an electron and becomes oxidized, thereby causing the reduction of the chlorine that acquired the lost electron.

The stoichiometric formulation of the oxidation-reduction reactions (also referred to as redox reactions) is considerably different from the formulation of all other reactions. A correct representation of the equation of an oxidation-reduction reaction requires introduction of the concept of the oxidation number. This number is a formal characteristic of each atom. The number is established on the basis of the charge that the atom seems to display in a compound—provided that the bonds with the other atoms have been formed exclusively as a result of the surrender (or the acquisition) of electrons.

In certain cases, the oxidation number is identified with the charge that the atom acquires when the molecule to which it belongs becomes dissociated in an aqueous solution and gives rise to ions. In other cases, the oxidation number is calculated in an arbitrary manner and does not correspond to any one ion of the element under consideration.

For example, the charge of the calcium in calcium chloride ($CaCl_2$) is equal to +2 and that of the chlorine is +1. These values are equal to the charge of the respective ions in solution. In covalent compounds, on the other hand, the atoms have a state of positive or negative oxidation, according to the electronegativity of the atoms under consideration. In methane, for example, the carbon atom is more electronegative than the hydrogen atoms. The hydrogen, therefore, will have an oxidation number of +1 and the oxidation number of the carbon will be −4.

The principal rules followed in assigning an oxidation number or state to a given substance are as follows:

1. The oxidation number of the atoms in the elementary state is zero, irrespective of the complexity of the molecule. Phosphorus, hydrogen, and sodium, for example, have tetratomic, diatomic, and monatomic molecules, respectively; but the oxidation number is equal to zero in all cases.

2. In an ion that consists only of a single atom, the oxidation number coincides with the electric charge possessed by the ion. In the case of the ion $Mg^{2+}$, for example, the oxidation number will be +2, and it will be +3 in the case of $Al^{3+}$.

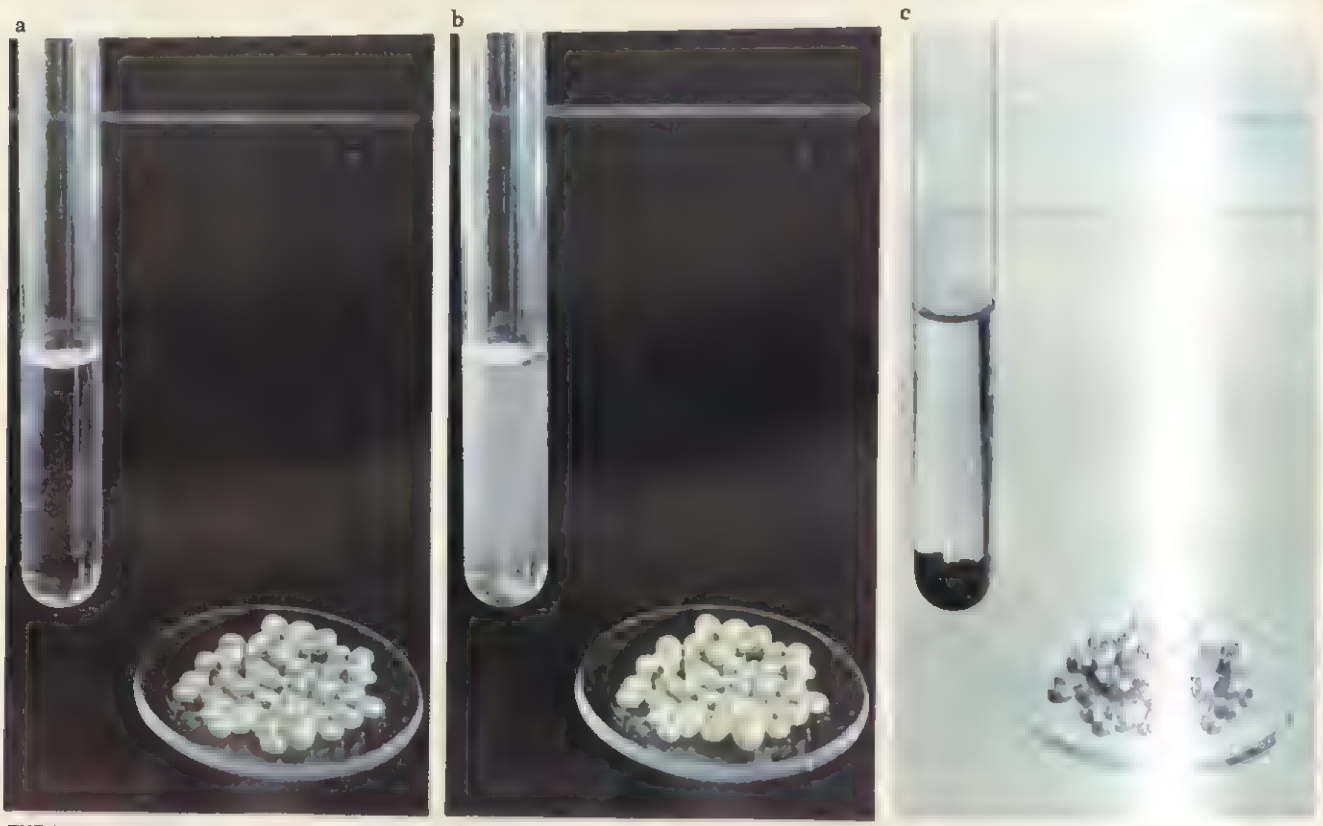
3. In the case of compounds or radicals that consist of several atoms, the two rules above must be specially applied. Hydrogen, for example, has an oxidation number of +1 (with the exception of hydrides, in which the oxidation number of the hydrogen is −1). Oxygen has an oxidation number of −2 (except in the case of peroxides and oxygen-fluorine bonds, fluorine being more electronegative than oxygen).

To attribute the oxidation numbers correctly in such cases, the two rules stated above will have to be applied in conformity with the following principle: in neutral molecules, the sum of the oxidation numbers of the constituent atoms must be zero; in complex ions, the sum of the oxidation numbers must be equal to the effective charge of the ion.

The following examples illustrate the three rules and their practical application.

The oxidation number of the nitrogen in nitric acid ($HNO_3$) is +5. It is determined as follows: the oxidation number of the hydrogen is +1; that of the three oxygen atoms is −6; that is, $-2 \times 3$. The oxidation number of the nitrogen must therefore be $+6 - 1$, or +5.

In potassium permanganate, $KMnO_4$, the manganese has an oxidation number of +7 because the potassium has a charge of +1; the charge of the four oxygen atoms is −8, and $(-8 + 1) = -7$. Oxidation-reduction equations can be balanced




**THE REDUCTION OF ZINC WITH A BISMUTH SALT**—Metallic zinc will precipitate metallic bismuth from a solution containing $Bi^{3+}$ ions, in accordance with the reaction

$$2Bi^{3+} + 3Zn = 3Zn^{2+} + 2Bi.$$

The test tube shown in illustration 1a contains a solution of a bismuth salt. Some granules of metallic zinc are in the watch glass on the right. If a granule of zinc is added to the solution in the test tube—as shown in illustration 1b—reduction to metallic bismuth begins immediately. In illustration 1c the black metallic bismuth is seen at the bottom of the test tube, the $Bi^{3+}$ ions having been completely reduced. The granules of zinc in the watch glass appear darker in illustration 1c only because of a change in light

by writing the equations relating to the reduction and oxidation reactions separately, then summing them in such a way that the number of free electrons is zero. An example is the reduction of the ferric ion ($Fe^{3+}$) into the ferrous ion ($Fe^{2+}$) as a result of contact with the stannous ion ($Sn^{2+}$), which is converted into the stannic ion ($Sn^{4+}$). The electronic processes are

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

and

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-.$$

If the first reaction is multiplied by 2 and then the two equations are added, the free electrons disappear and the exact expression of the oxidation-reduction process is

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}.$$

A more complex example is provided by the reaction between potassium permanganate, $KMnO_4$, and ferrous sulfate $FeSO_4$,

$$2KMnO_4 + 10FeSO_4 + 8H_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

The manganese (which has an oxidation number of +7 in the permanganate) passes to an oxidation number of +2 in the manganese sulfate, while the ferrous ion (with an oxidation number of +2) becomes a ferric ion with an oxidation number of +3,

$$MnO_4^- + 5e^- \rightarrow Mn^{2+} \ (Mn^{7+} \rightarrow Mn^{8+})$$

and

$$Fe^{2+} \rightarrow Fe^{3+} + e^-.$$

To calculate the reaction coefficients, the respective reactions of oxidation and reduction must be balanced. To do this, use is made of the fact that in an acid environment, hydrogen reacts with oxygen to form $H_2O$ and that this oxygen does not remain bound to the oxidizing agent because of the reduction of the oxidation number. The coefficients of the two reactions (oxidation and reduction) must, therefore, be multiplied by suitable values to ensure that the number of exchanged electrons is equal. If the two equations obtained are added, the reaction in ion form—with its exact stoichiometric coefficients—will be obtained. The manganese, in passing from a state of oxidation of +7 to a state of oxidation of +2, acquires five electrons that will subsequently be subtracted from the five iron atoms, which will thus pass from $Fe^{2+}$ to $Fe^{3+}$ by the following reactions:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

and

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-.$$

If all terms on the right are added, and similarly, those on the left, the reaction in ion form and, eventually, in molecular form is

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}.$$

# OXIDIZING AGENTS AND REDUCING AGENTS

## fundamental concepts and particular phenomena

In addition to the normal reactions of oxidation and reduction, there are also reactions in which the same element behaves both as a reducing agent and as an oxidizing agent. The phenomenon of simultaneous oxidation and reduction of the same element is called disproportionation, or dismutation. The reactions are called internal oxidation and reduction reactions. An example is the formation of sodium hypochlorite and sodium chloride from gaseous chlorine and sodium hydroxide.

$$Cl_2 + 2NaOH \rightarrow NaClO + NaCl + H_2O$$

In this reaction the chlorine passes from an oxidation number of 0 to an oxidation number of +1 in the hypochlorite and −1 in the chloride.

Thus, the same element has increased its oxidation number in the formation of one compound and reduced its oxidation number in the formation of another compound.

### SELF-OXIDATION

The rather rare phenomenon of self-oxidation is somewhat analogous to catalytic action, although there are important differences. Self-oxidation is illustrated by the action of two solutions: sodium arsenite ($Na_3AsO_3$) and sodium sulfite ($Na_2SO_3$). If both are exposed to atmospheric oxygen, the sodium sulfite is oxidized to sodium sulfate ($Na_2SO_4$) and the sodium arsenite undergoes no change. If the resulting two compounds are then mixed, and atmospheric oxygen is bubbled through the solution, the arsenite is oxidized to arsenate ($Na_3AsO_4$). For each molecule of sulfite previously oxidized to sulfate, a molecule of arsenite is oxidized to arsenate. The mechanism is as follows: a molecule of oxygen reacts with the sulfite, forming a complex and unstable sulfate; this compound then transfers an oxygen atom to the arsenite, oxidizing it to arsenate. This action is similar to that of a catalyst, but is different in that the quantity of oxygen ceded by a self-oxidizing agent is not unlimited (as it is with a catalyst), but can never be greater than half the amount of absorbed oxygen—unless, during the process, the structure of the self-oxidizing agent is altered by other reactions.

### GRAM EQUIVALENTS IN OXIDATION AND REDUCTION REACTIONS

In acid-base neutralization reactions, equivalent weights are calculated on the basis of the hydrogen atoms displaced. In oxidation-reduction reactions, the concepts of oxidation equivalent and reduction equivalent are introduced. The oxidizing or reducing capacity of a given substance is a direct function of the number of electrons that are displaced during the process. Thus, the oxidation (or reduction) equivalent is found by dividing the molecular weight of the molecule by the number of electrons lost or acquired during the oxidation or reduction.

In the case of the oxidation of ferrous sulfate by means of permanganate, the reaction is: $5Fe^{2-} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$. The equivalent weight of the sulfate is given by

$$\frac{FeSO_4}{1} = FeSO_4 = 151.9.$$

The equivalent weight of potassium permanganate in acid solution is given by the formula:

$$\frac{KMnO_4}{5} = \frac{158.03}{5} = 31.6.$$

Furthermore, since the equivalent weight of a substance depends on the reaction under consideration, the same substance can have different oxidation and reduction equivalents for different reactions. An example of this is provided by sulfur in the following discussion.

In the process where hydrogen sulfide, $H_2S$ (where sulfur has an oxidation number of −2), is oxidized to sulfur trioxide, $SO_3$ (where sulfur has an oxidation number of +6), the oxidation equivalent of the sulfur is S/8—since sulfur loses eight electrons.

On the other hand, in the reaction in which sulfur is oxidized to sulfur dioxide, $SO_2$, the oxidation equivalent of the sulfur is S/4 because sulfur loses only four electrons. Finally, in the oxidation of sulfur dioxide to sulfur trioxide, the equivalent is S/2.

The reactions of oxidizing and reducing agents with each other are based on their equivalent weights. A normal solution of these two agents is one having one gram equivalent in one liter—as with potassium permanganate in an acid environment, where the normal solution is one with 31.6 g of the compound in one liter of the solution.

**THE DISMUTATION OF POTASSIUM MANGANATE**—An example of a disproportionation reaction is the reaction of $K_2MnO_4$ in water. Potassium manganate dismutates by depositing $MnO_2$. The solution turns violet due to the presence of $KMnO_4$ (potassium permanganate):

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

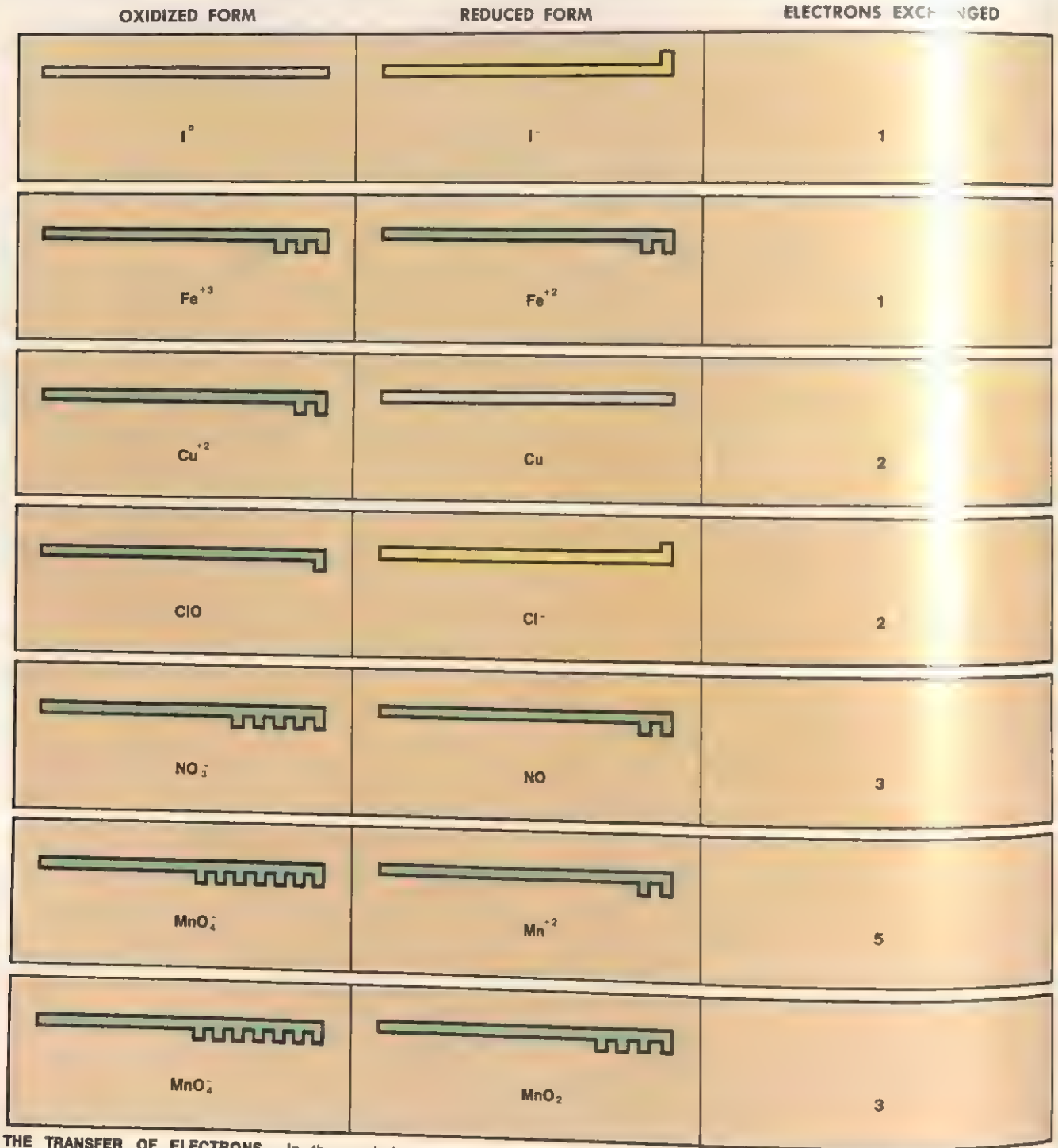
## OXIDIZING AND REDUCING AGENTS

A substance can act as an oxidizing or reducing agent, depending on the temperature, its concentration, and the substances with which it is made to react. The most common strong oxidizing agents are oxygen itself, potassium permanganate, potassium dichromate, the halogens, hydrogen peroxide, other peroxides, and concentrated nitric acid. Dilute nitric acid and concentrated sulfuric acid are oxidizing agents of medium strength. If weak oxidizing agents are needed, silver oxide and cupric oxide may be used.

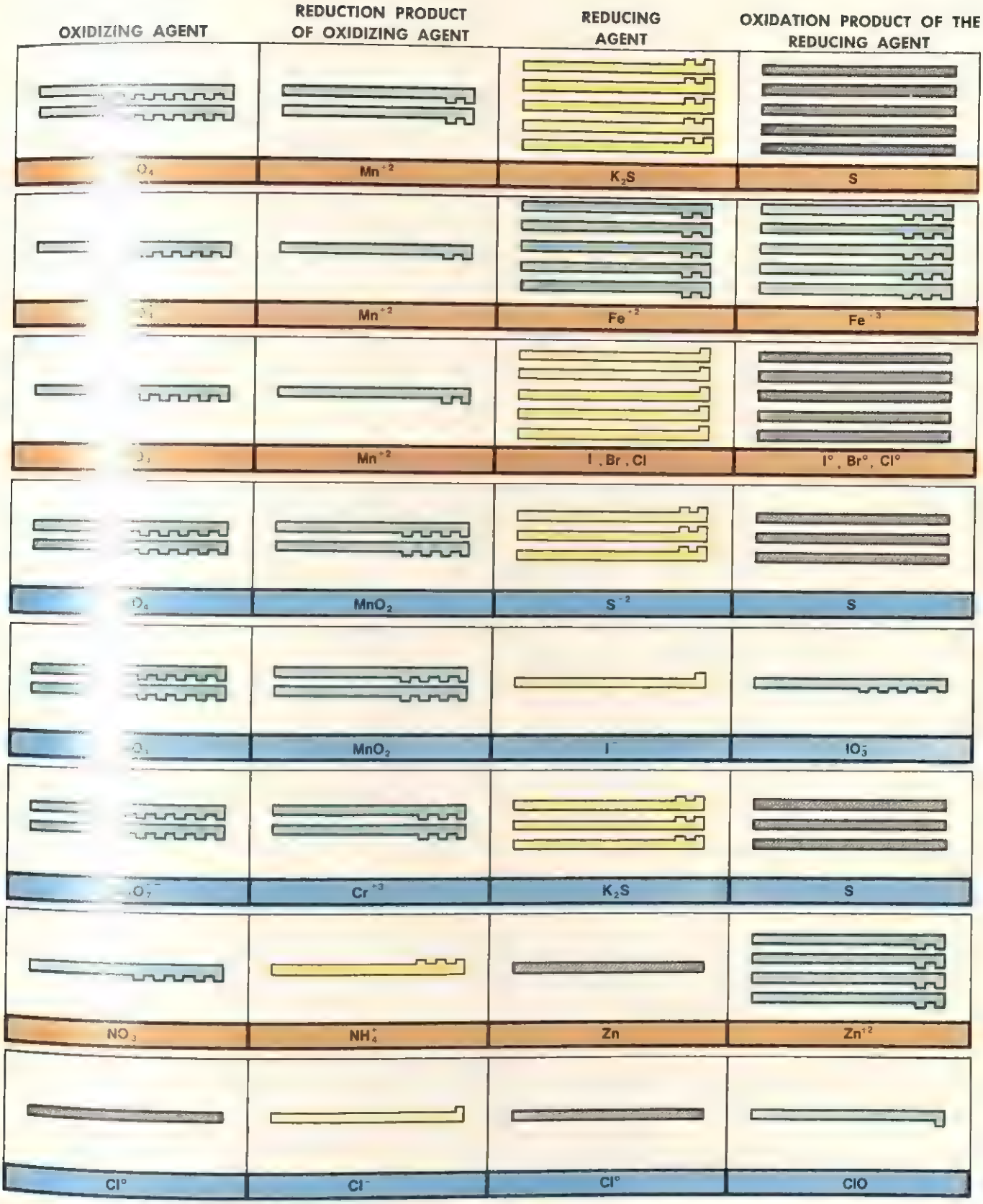
The oxidizing strength of the halogens is as follows:

fluorine > chlorine > bromine > iodine

In general, nonmetallic elements are oxidizing agents, while metallic elements are reducing agents. The most common reducing agents are active hydrogen (hydrogen liberated by the action of metals on acids), stannous chloride, carbon, and hydriodic acid.




**THE TRANSFER OF ELECTRONS** — In the table shown here, a simple bar represents an oxidation number of zero; bars with teeth pointing downward represent a positive oxidation number; and bars with teeth pointing upward represent a negative oxidation number. The table illustrates the number of electrons exchanged in going from an oxidized state to a reduced state.




**OXIDATION-REDUCTION REACTIONS** — This table uses the same symbolism as illustration 2 in order to show a series of partial oxidation-reduction reactions. Reactions that occur in acidic conditions are shown against an orange background; those occurring in alkaline conditions are shown in blue. The first case is an example that needs to be balanced. The oxidation reaction ($MnO_4^- + 5e \rightarrow Mn^{2+}$) is multiplied by 2 and the reduction reaction ($S^{2-} \rightarrow S + 2e$) by 5; thus, the number of electrons gained equals the number lost: 10.

# ACIDS AND BASES | chemical antagonists

No chemist would ever peer into a glass of water to see if he could find a broken molecule or two. Chemists, however, do something not appreciably different from this. What is more, they are able to make fairly accurate measurements of the extent of the "breakage" or, to put it more exactly, ionization. The reaction involved is $H_2O \rightarrow H^+ + OH^-$. This is the ionization, or splitting, of a water molecule into one hydrogen ion ($H^+$) and one hydroxyl ion ($OH^-$).

As it stands, however, this reaction is incorrect, for it is not possible for a hydrogen ion to exist in isolation in a solution. What then does $H^+$ represent? The hydrogen atom, the simplest of all atoms, consists of a one-proton nucleus. A hydrogen ion is merely a hydrogen atom that has had the electron stripped away, leaving just the proton.

A proton or $H^+$ ion is an extremely small particle with a very high concentration of electric charge. The electron with its negative charge is no longer present to exert a neutralizing effect. As a result, the $H^+$ particle forms loose electrostatic bonds with one or more un-ionized water molecules. This occurs because water molecules are polar; that is, their internal charge is unevenly distributed so that one part of the molecule is positive and the other part negative. What happens, therefore, is that the hydrogen ion, with its very high positive charge, is attracted to the negative end of the polar water molecule. The correct form of the reaction is thus

$$H_2O + H_2O \rightarrow \overbrace{H^+ \text{---} H_2O}^{H_3O^+} + OH^-.$$

$H_3O^+$ groups are called hydronium ions. A more general formula, taking into account the fact that more than one $H_2O$ molecule may associate with the $H^+$ particle, is $H(H_2O)_n^+$.

Hydroxyl ($OH^-$) ions also associate with water molecules. In chemical terms, the $H^+$ ion and the $OH^-$ ion are said to be hydrated.

This phenomenon, however, is not restricted to $H^+$ and $OH^-$ ions. All ions in aqueous solutions, whether positively or

1

**ACIDS AND BASES**—The illustration shows a variety of different acids and bases, each in its own characteristic bottle. Some of the bottles are transparent and some are black. The black bottles are used to store substances that are sensitive to light. Other bottles are made of polyethylene, a synthetic plastic highly resistant to corrosion from chemical agents.

2

**$H_2O$**—This is the orientation in space of the atoms in a molecule of water. The large atom of oxygen is bonded to the two smaller hydrogen atoms at the side. The bond angle is 105°.

negatively ch[illegible]d, should be regarded as being hyd[illegible] that is, surrounded by a shell of att[illegible]d water molecules.

Hydratio[illegible]ons is of considerable importance [illegible]nust always be taken into accou[illegible]lution reactions. Why, for exampl[illegible] ordinary salt dissolve in a glass o[illegible] The alchemists would have replie[illegible] question with a salvo of magical [illegible]s. Modern chemistry fortunately [illegible]re sophisticated weapons in its [illegible]. nd can give a more convincing [illegible] What exactly happens when [illegible]l of sodium chloride (common s[illegible] dropped into a glass of water? C[illegible] salt is an ionic solid; that is, it co[illegible]f a three-dimensional array of alt[illegible]; positive and negative ions attracti[illegible]nother. By hydrating the ions, th[illegible]ecules of water overcome the fo[illegible] attraction in the solid state and permit the crystal to dissolve. To be even more precise, $H_2O$ molecules accumulate around a negative chloride ion ($Cl^-$) with their positive parts pointing toward the $Cl^-$ ion. As a result the $Cl^-$ ion is pulled away from the solid and hydrated--it has gone into solution. The same thing happens to an $Na^+$ ion. In this case, however, the $H_2O$ molecules point their negative parts toward the $Na^+$ ion. The ion thus goes into solution in hydrated form. (Illustration 3 represents this process.)

The number of positive ions present in the NaCl solution will clearly equal the number of negative ions. Moreover, if the NaCl solute is taken out of the solution, the resulting pure water will contain an equal number of hydroxyl and hydrogen ions, as well as a very large number of un-ionized $H_2O$ molecules. One useful way to express these concentrations in quantitative form is:

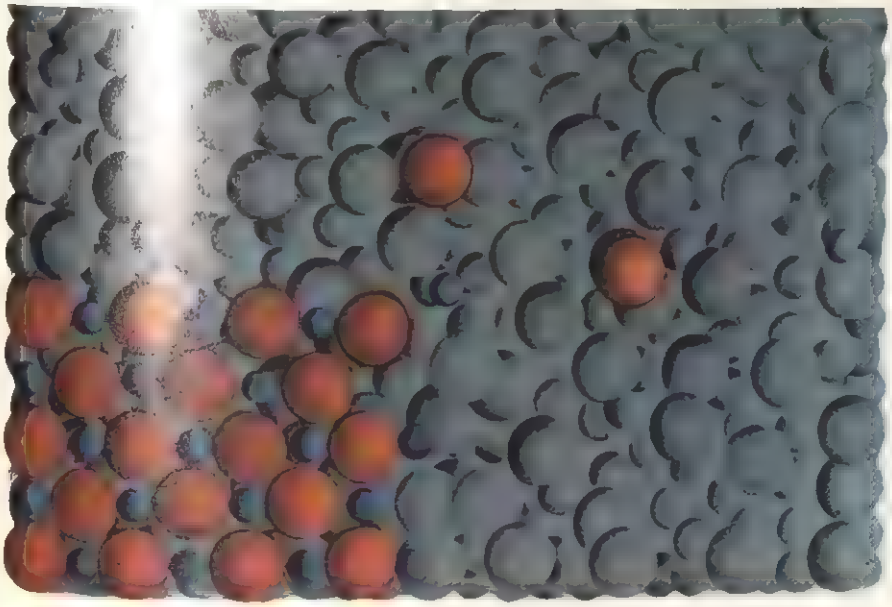
$$\frac{[H^+]\,[OH^-]}{[H_2O]} = K$$

The terms in brackets represent the concentrations of the ions and molecules; the letter $K$ is a constant.

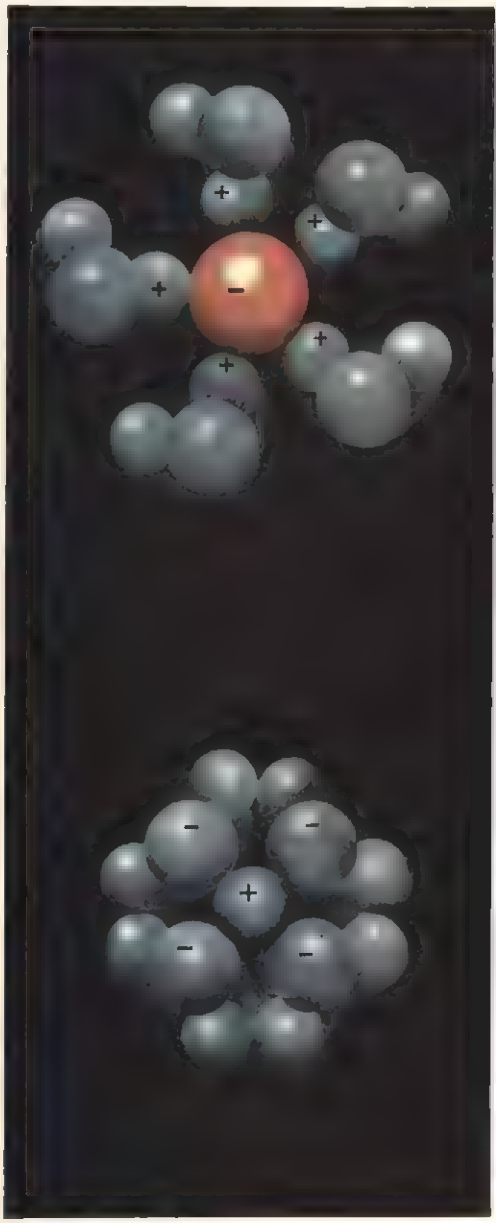
**SOLUBILITY**--[illegible]solid, the m[illegible] forces of att[illegible] drated ions a[illegible] shows a frag[illegible] mon salt (N[illegible] water. The w[illegible] lons away fro[illegible]

[illegible]drating the lons of the [illegible] of water neutralize the [illegible] between them. The hy- [illegible]n solution. Illustration 3a [illegible]e crystal lattice of com- [illegible]unded by molecules of [illegible]ecules tend to pull the [illegible]id. Illustration 3b shows two ions, one of sodium (blue) and the other of chlorine (red), surrounded by molecules of water. The chloride lon, negatively charged, is surrounded by the positive parts of the polar water molecules, while the sodium lon, positively charged, is surrounded by the negative parts of the polar water molecules.

3a



3b



4

**THE INDICATOR TEST**—The test tubes contain neutral, acid, and basic solutions. The indicator in the tube at the left remains yellow, showing that the solution is neutral. The paper in the tube at the top right has turned red, showing the presence of an acid. The blue color of the paper in the tube at the bottom right indicates the presence of a base.

By rearranging terms, the equation becomes $K[H_2O] = [H^+][OH^-]$. Since the concentration of water in dilute solutions is essentially constant, however, the term $K[H_2O]$ becomes a new constant—$K_w$. This is called the ionization constant of water. The value of this constant at 25°C is known: $K_w = 1 \times 10^{-14}$. The equation thus becomes: $1 \times 10^{-14} = [H^+][OH^-]$. Since among other things, however, the concentrations of $H^+$ and $OH^-$ are equal, the final form is $[H^+] = [OH^-] = 1 \times 10^{-7}$.

This figure reveals the very small degree of ionization that takes place in water. A liter of water, in fact, contains but one $H^+$ ion and one $OH^-$ ion for every 554 million molecules of water. The symbol $H^+$ is merely a convenient shorthand for that of the hydrated ion: $H(H_2O)_n^+$.

When a substance such as NaCl is added to water, the $H^+$ and $OH^-$ concentrations are in no way changed because salt contains neither one nor the other. If, on the other hand, a substance such as HCl is added to water, additional hydrated $H^+$ ions will go into solution. The concentration of $H^+$ ions in the solution, therefore, will no longer be $1 \times 10^{-7}$, but considerably higher. The concentration of $OH^-$ ions will decrease, however, since the ionization constant $K_w$ must remain constant. In other words, $H_2O$ molecules will recombine from $H^+$ and $OH^-$ ions and remove both $H^+$ and $OH^-$ ions from the solution. Hydrogen ions, introduced when HCl was added, will thus be present in much greater numbers than hydroxyl ions.

The same thing happens to the concentration of $OH^-$ ions if a substance such as NaOH is added to water. The result is an excess of $OH^-$ ions coupled with a decrease in the concentration of $H^+$ ions.

These two types of compounds behave differently when dissolved in water. The first type produces an increase in hydrogen ion concentration, and the second types increases hydroxyl ion concentration. These phenomena are the basis for

**MAGNESIUM HYDROXIDE**—The test tube contains a cloudy, milky suspension of magnesium hydroxide, a base obtained by reacting solutions of magnesium sulfate with sodium hydroxide. The reaction is

$$2NaOH + MgSO_4 \rightarrow Mg(OH)_2 + Na_2SO_4.$$

**ACIDS**—Two acids with uniquely characteristic properties. Illustration 6a shows a beaker containing a solution topped by a white foam-like mass, benzoic acid. Because it is lighter than water, the acid floats on the surface in a thick white layer. Illustration 6b shows the beautiful green flames that develop when boric acid is treated with a small amount of alcohol.

6a

6b

one definit[illegible] two types of compounds of great im[illegible]ance to chemistry: acids and bases.

Any subst[illegible] capable of increasing the $H^+$ ion c[illegible]entration in a solution is said to be a[illegible]cid, and any substance capable of [illegible]sing $OH^-$ ion concentration is sa[illegible] be a base. Water is regarded as n[illegible]l; it contains an equal number of hydrogen and hydroxyl ions.

Acids and bases have distinctively different properties. Acids have a special sour taste and a pungent odor, while bases have a bitter taste and a slippery consistency. The chief difference from the point of view of analysis, however, is that acids and bases color indicators differently. A yellow universal indicator will turn bright red in the presence of an acid and blue in the presence of a base (Illustration 4).

# THE STRENGTH OF ACIDS AND BASES

## fighting each other to a standstill

As presented in a previous article, the chief difference between acids and bases is that acids yield hydrogen ions ($H^+$) whereas bases yield hydroxyl ions ($OH^-$) in aqueous solutions. Some acids and some bases are stronger than others. No one would dream of using hydrochloric acid or sulfuric acid as an eyewash instead of boric acid, or of swallowing a dose of caustic soda, instead of bicarbonate of soda, for an upset stomach. Common knowledge, however, is only a rough-and-ready guide to the strength of acids and bases. More precise information taken from chemistry is needed.

What happens when each of three solutions with the same molar concentrations (the same number of moles per liter)—hydrochloric acid, HCl, hydrobromic acid, HBr, and hydriodic acid, HI—is reacted with an equal quantity of zinc? Those elements that precede hydrogen in the electrochemical series displace it from acid solutions in which it is present as $H^+$ ion. The hydrogen is thus liberated in gaseous form ($H_2$):

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2.$$

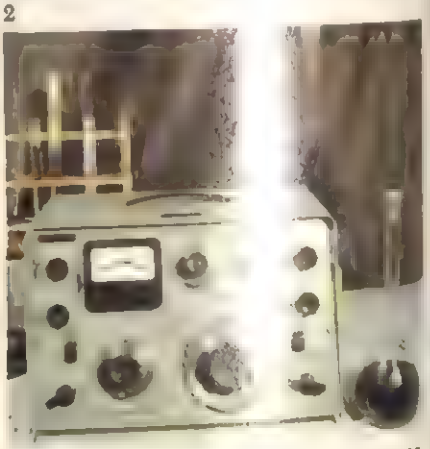
If equal volumes of the acids are used, and if the hydrogen liberated is measured, it will be found that the quantity of $H_2$ liberated by the HI system is slightly greater than the quantity liberated by the HBr system (assuming equal reaction times for all three systems), which in turn is greater than the quantity liberated by the HCl system. Since equal volumes of solutions with equal molar concentrations contain the same number of molecules (each of which ionizes to give an $H^+$ ion), the greater reactivity of the HI reaction system must be the result of a greater number of $H^+$ ions than in the other systems. On this basis, HI is considered a stronger acid than HBr, which is stronger than HCl. The strength of an acid is thus measured in terms of the hydrogen ion concentration of the solution. The scale of acid strength ranges from very strong acids—HI, HBr,

1a

**STRENGTH OF AN ACID**—A small amount of sulfuric acid poured over any organic substance is enough to demonstrate the strength and dehydrating power of the acid. Nothing remains of the treated parts except charred holes. Sulfuric acid is a strong acid, in contrast to boric acid, which can be applied safely to the skin. The photograph below shows a geyser, a typical source of boric acid.

1b

2



**pH-METER**—This instrument is used to measure the pH of both acids and bases.

3a

3b

3c

**IONIC OXIDES** These compounds are generally solid at room temperature. One example of an ionic, or basic, oxide is calcium oxide (CaO), better known as quicklime (illustration 3a). When poured into a beaker of water (illustration 3b), it produces a basic solution (illustration 3c) containing $Ca(OH)_2$. The milky-white appearance is due to undissolved $Ca(OH)_2$.

HCl—through an intermediate range, down to the weak acids (boric acid), and finally to the very weak acids (hydrocyanic acid). The word weak means that the acid is less ionized.

The strength of bases is assessed by applying the same reasoning to hydroxyl ($OH^-$) ions.

The pH of a solution is defined as the negative logarithm of the concentration of hydrogen ions in the solution. In equation form, this is:

$$pH = -\log [H^+].$$

Suppose, for example, that a solution contains one thousandth of a gram-ion ($.001 = 10^{-3}$ g-ion) of hydrogen in one liter of solution. Its pH is thus

$$pH = -\log 10^{-3} = 3.$$

Conversely, a solution whose pH = 8 will have a hydrogen-ion concentration equal to $10^{-8}$ g-ion/l. In the case of neutral solutions such as water, the concentration of hydrogen ions is equal to the concentration of hydroxyl ions:

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}$$

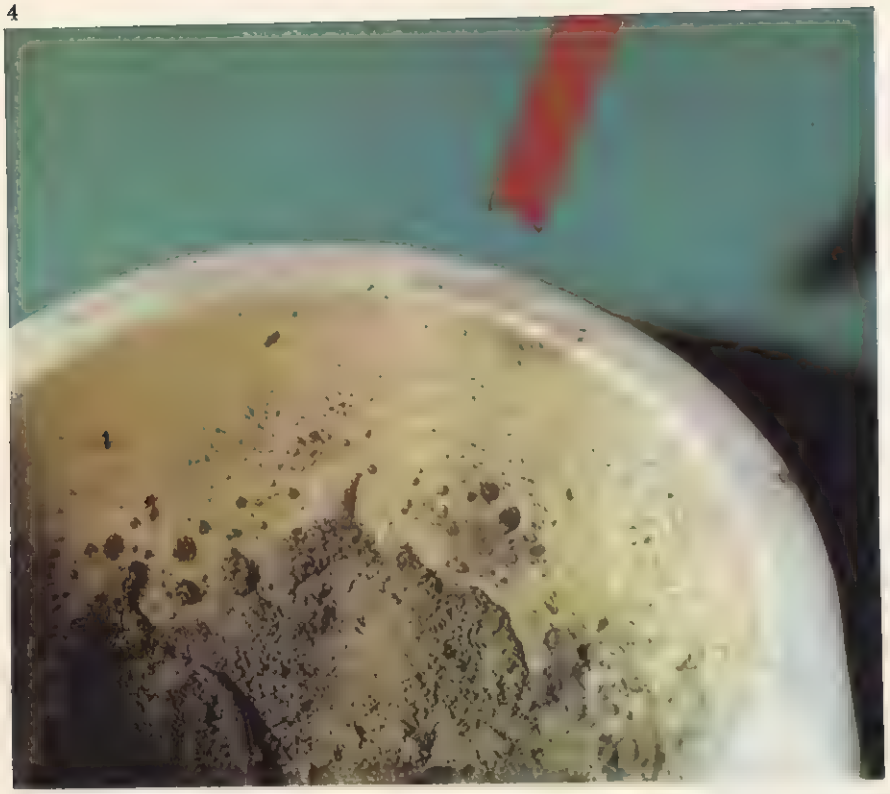
The pH of water is therefore 7. For acidic solutions it is less than 7, and for basic solutions, greater than 7. The concentration of a strong acid provides the concentration of $H^+$ ion, which gives the pH value. In the case of a strong base the concentration is in terms of $OH^-$ ions. Thus, to obtain the $H^+$ ion concentration and the pH, the following equation is used:

$$[H^+]\,[OH^-] = K_w = 1 \times 10^{-14}$$

where $K_w$ is the dissociation constant for water. Therefore,

$$[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}.$$

4



**ACID ANHYDRIDES**—These oxides color a water-moistened litmus indicator red, and produce acid solutions. An example is sulfur dioxide ($SO_2$). Obtained by burning sulfur, this compound reacts with the water in the indicator to produce sulfurous acid ($H_2SO_3$), which turns the indicator red.

To solve for $[H^+]$, the value of $[OH^-]$ is substituted into the equation, which is then solved for $[H^+]$.

pH may also be determined by using an instrument called a pH-meter. Another way is to use indicators that take on a characteristic color indicative of the pH value.

## THE ORIGIN OF ACIDS AND BASES

How are acids and bases formed? All elements except the noble gases combine with oxygen to produce oxides. Some of these oxides contain ionic bonds while others contain covalent bonds.

Ionic oxides, like all ionic substances, are solids at room temperature. They are generally formed from alkali and alkaline-earth metals. These substances are called basic oxides, because their solutions produce hydroxyl ions.

$$CaO + H_2O \rightarrow Ca(OH)_2 \rightleftarrows Ca^{2+} + 2OH^-$$

The elements to the right of the periodic table form covalent oxides called acid anhydrides. These substances produce acids in solution. Thus sulfur trioxide, $SO_3$, forms sulfuric acid with water according to the reaction:

$$SO_3 + H_2O \rightarrow H_2SO_4 \rightleftarrows 2H^+ + SO_4^{2-}.$$

## AMPHOTERIC SUBSTANCES

Some oxides, generally those formed with elements from the center of the periodic table, have both acidic and basic properties. Such substances are said to be amphoteric.

Aluminum hydroxide, for example, behaves differently in the presence of acids as compared to bases:

$$Al(OH)_3 + 3OH^- \rightarrow AlO_3^{3-} + 3H_2O \quad (1)$$
$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O \quad (2)$$

The first reaction produces the anion $AlO_3^{3-}$, the second the cation $Al^{3+}$. The explanation of this phenomenon lies in the fact that several bonds in the aluminum hydroxide molecule may be broken. Addition of an acid solution ($H^+$ ions) causes a break in the Al—O bonds, with the hydrogen ions then combining with the hydroxide ions to form water:

$$\begin{array}{c} OH + H^+ \\ Al{-}OH + H^+ \rightarrow Al^{3+} + 3H_2O. \\ OH + H^+ \end{array}$$

In the presence of hydroxyl ($OH^-$) ions, however, the bond between the oxygen and the hydrogen is the one that breaks. As a result, $OH^-$ ions join with the $H^+$ ions and form molecules of water. The other product of the reaction is the aluminate ion $AlO_3^{3-}$;

$$\begin{array}{cc} OH + OH^- & O \\ Al{-}OH + OH^- \rightarrow & Al{-}O^- \quad 3H_2O. \\ OH + OH^- & O \end{array}$$

## NEUTRALIZATION

The tendency of water to ionize is very small. This means, therefore, that $H^+$ and $OH^-$ ions have a marked affinity for each other. That is, they tend to recombine immediately. But acids yield hydrogen ($H^+$) ions and bases yield hydroxyl ($OH^-$) ions in solution. Thus, what happens when an acid (HCl, for example) and a base (NaOH, for example) are combined in solution is easy to predict. The $H^+$ ions of the acid combine with the $OH^-$ ions of the base to form water. The $Na^+$ ions produced by the dissociation of the base and the $Cl^-$ ions produced by the ionization of the acid remain in solution.

This combination of $H^+$ ions and $OH^-$ ions is the so-called neutralization reaction. Neutralization is thus the reaction of an acid and a base in solution to form water and a salt. The salt in the example above consists of the $Na^+$ and $Cl^-$ ions. These ions are hydrated, that is, surrounded by molecules of water in solution. If the solution is evaporated, however, the molecules of water surrounding the ions are driven off. The ions then recombine to form crystals of sodium chloride, NaCl. The reaction of an acid with a base thus gives rise to a new series of compounds—salts. The actual reaction in neutralization, however, is simply:

$$H^+ + OH^- \rightarrow H_2O.$$

The form

$$HCl + NaOH \rightarrow H_2O + NaCl$$

is incorrect because it implies that the $Na^+$ and $Cl^-$ ions take part in the neutralization reaction. This is not the case at all.

# pH | the degree of acidity or alkalinity

Water is the sol[illegible]t most frequently used in preparing s[illegible]tions. A water molecule is produced [illegible] two hydrogen atoms are joined to [illegible]ygen atom. This molecule is repre[illegible]d by the symbol $H_2O$. After extensi[illegible]urification, water has an ion condu[illegible]ty that ceases to vary. As the table [illegible]s, this conductivity has different valu[illegible]ccording to the temperature of t[illegible]quid.

CONDU[illegible]ITY VALUES OF PURE W[illegible] AT DIFFERENT TI[illegible]RATURES

| | |
|---|---|
| at 18° C | 0[illegible] · $10^{-6}$ ohm$^{-1}$ cm$^{-1}$ |
| at 25° C | 0[illegible] · $10^{-6}$ ohm$^{-1}$ cm$^{-1}$ |
| at 50° C | 0[illegible] · $10^{-6}$ ohm$^{-1}$ cm$^{-1}$ |

The very sma[illegible]quantity of ions present indicates the [illegible] electrical conductivity of pure wate[illegible]ater can be dissociated as follows:

$$H_2O \rightleftharpoons H^+ + OH^-. \quad (1)$$

With the te[illegible]ature constant, a small percentage o[illegible]) molecules dissociates to provide H[illegible]drogen ions and $OH^-$ hydroxyl ion[illegible] solution. By applying the laws of [illegible] action to (1), it can be shown th[illegible]e product of the concentration o[illegible]$^+$] hydrogen ions and $[OH^-]$ hydr[illegible]ions in a liter of water,

$$[H[illegible]OH^-] = K_w, \quad (2)$$

called the ion[illegible]oduct of water, is a constant at const[illegible]temperature.

If the con[illegible]ntration of $[H^+]$ and $[OH^-]$ is ex[illegible]ssed in gram ions per liter, the valu[illegible] obtained is about $10^{-14}$ at 25° C (77° F) for $K_w$. This concentration is equal to a solution in which one liter contains a number of grams of individual ions equal to its weight.

VALUES OF THE ION PRODUCT OF WATER ($K_w$) AS A FUNCTION OF TEMPERATURE

| (gram ions per liter) | |
|---|---|
| at 0° C | $K_w = 0.113 \cdot 10^{-14}$ |
| at 25° C | $K_w = 1.007 \cdot 10^{-14}$ |
| at 50° C | $K_w = 5.480 \cdot 10^{-14}$ |

This value permits calculation of the concentration of hydrogen ions in pure water. In this case, it clearly follows from (1) that the formation of each hydrogen ion is accompanied by the formation of a hydroxyl ion, in other words, $[H^+] = [OH^-]$. It therefore follows from (2) that

$$[H^+]^2 = 10^{-14},$$

in other words

$$[H^+] = 10^{-7} \text{ gram ions/liter.} \quad (3)$$

When water dissolves substances that can free hydrogen ions (called acids), or hydroxyl ions (called bases), the value for the concentration of hydrogen ions varies a great deal from that derivable from (3).

An experiment may require a liter of aqueous solution in which one mole of hydrochloric acid has been dissolved. Hydrochloric acid is a strong acid that can be completely decomposed in solution so that, in effect, the solution will contain only $H^+$ and $Cl^-$ ions. Here the concentration of $H^+$ ions is equal to 1. It follows from (2) that the $[OH^-]$ concentration should be equal to:

$$\frac{10^{-14}}{[H^+]} = 10^{-14} \text{ gram ions/liter.} \quad (4)$$

Obviously, the numbers representing the concentration of hydrogen and hydroxyl ions involve using powers with exponents that are often negative. If these powers were not used, writing down these relations would be very awkward. For pure water at 25° C (77° F), given that $[H^+]^2 = 10^{-14}$, the written formula would be $[H^+] = 0.000,000,1 = 10^{-7}$. In the case of hydrochloric acid in solution (4), it would become

$$[OH^-] = 0.000,000,000,000,01 = 10^{-14}.$$

## DEFINITION OF pH

The pH of an aqueous solution is defined as the decimal logarithm with the sign changed of the concentration of hydrogen ions. It is important to remember that the decimal logarithm of a power to base 10 is equal to the exponent of the power. Thus, $\log 10^a = a$. In other words,

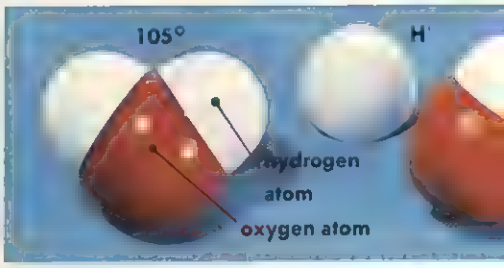
$$pH \equiv -\log[H^+]. \quad (5)$$

This quantity, apparently much more complicated than the simple concentration of hydrogen ions $[H^+]$, makes it much simpler to describe a solution's acidity or alkalinity because small numbers can be used. For normal cases, the pH scale extends from 0 to 14. It is easy to calculate the pH of pure water at 25° C (77° F) from (3) and (5). It is

$$pH = -\log 10^{-7} = -(-7) = 7. \quad (6)$$

Since pure water is completely neutral (the condition $[H^+] = [OH^-]$ holds for pure water), it is clear that, for a temperature of 25° C (77° F), pH = 7 corresponds to what is called the neutrality point. Values of pH above 7, and normally falling within the interval between 7 and 14, represent conditions of alkalinity ($[H^+] < [OH^-]$) that increase the further away it moves from 7. Values for pH below 7, normally included in the interval between 7 and 0, represent conditions of acidity ($[H^+] > [OH^-]$) that increase as the numerical value of pH gets smaller.

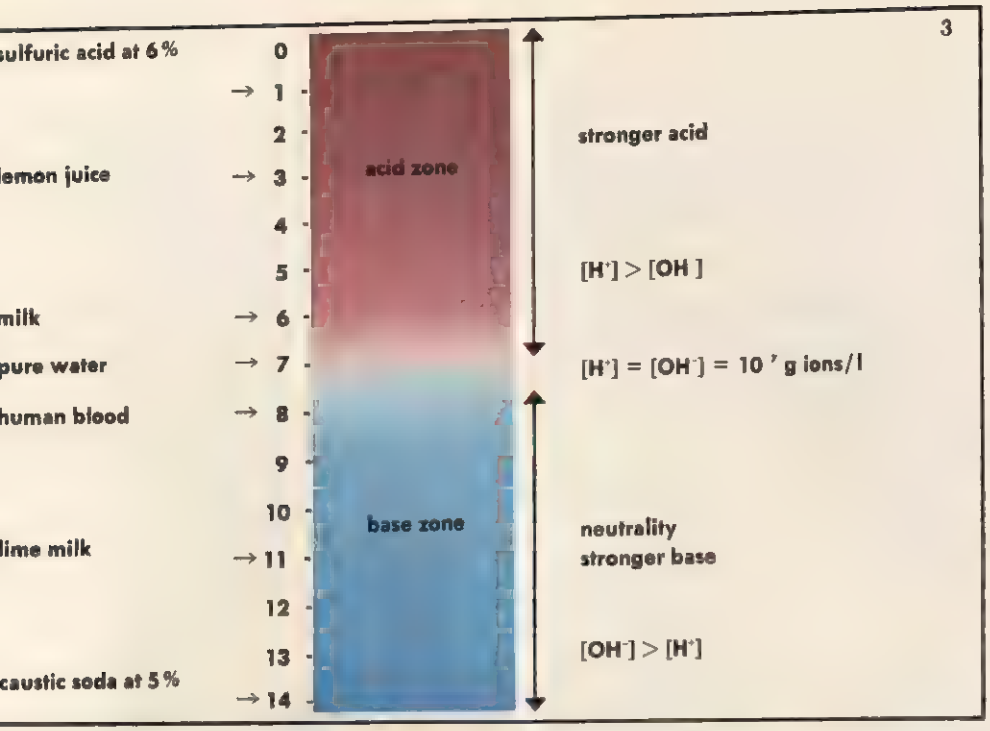
1




**WATER MOLECULE**—A water molecule consists of an oxygen atom and two hydrogen atoms forming an angle of 105°. When they dissociate, they split up into $H^+$ and $OH^-$ ions. **THE CONDUCTIVITY OF WATER**—Water has a low degree of conductivity, as indicated by the different positions of the needle in illustrations 2a and 2b.

2a

2b




It is very important to note that, since the pH scale is logarithmic, the concentration of hydrogen ions is multiplied (or divided) by ten for each unit change in the value of pH. Thus, if a solution moves from pH 6 to pH 5, the concentration of hydrogen ions is ten times greater. Moving from pH 6 to pH 4 increases the concentration one hundred times, and so on.

Finally, it should be noted that for various practical purposes in analytical chemistry, biology and so on, many properties in a solution are characterized almost uniquely by the pH value. Knowing a solution's pH is often more important than knowing, for example, its chemical composition, particularly in relation to the speed with which precipitates are formed (flocculation), the degree of corrosiveness, and so on.

## BUFFER SOLUTIONS

Buffer solutions stop sharp changes in pH; the pH value of a buffer solution will vary very little if small quantities of even a strong acid or base are added. The higher the tendency of the solution to keep its pH value, the higher its buffering power. Buffer solutions are fairly widespread in nature. There is a buffering system in human blood that keeps its pH at 7.35. A buffer normally consists of an aqueous solution of a weak acid and its salt with a strong base or a weak base and its salt with a strong acid.

For example, study the buffer, acetic acid-sodium acetate. Acetic acid is defined as a weak acid because in aqueous solution, it gives the equilibrium

$$CH_3{-}COOH \rightleftarrows CH_3{-}CO^- + H^+, \quad (7)$$

in which a limited number of hydrogen ions is found. Sodium acetate is a salt obtained by neutralizing acetic acid with the strong base, NaOH. In water solution, sodium acetate dissociates completely into its components

$$CH_3{-}COO^- + Na^+ \quad (8)$$

In the buffer solution, apart from the $H^+$ and $OH^-$ ions, there are also the types

$$CH_3{-}COOH \text{ and } CH_3{-}COO^-.$$

If a small quantity of acid is now added to the solution, the hydrogen ions freed by the acid are immediately buffered by the $CH_3COO^-$ particles belonging to the reaction:

$$CH_3{-}COO^- + H^+ \rightarrow CH_3{-}COOH. \quad (9)$$

But, if a small quantity of base is added, the $OH^-$ ions introduced are faced by the reaction:

$$CH_3{-}COOH + OH^- \rightarrow CH_3{-}COO^- + H_2O. \quad (10)$$

To sum up, adding an acid or a base alters the value of the relationship $CH_3{-}COO^- / CH_3{-}COOH$ without causing variations in the solution's pH.

**BUFFER SOLUTIONS**—Even if small quantities of a strong base or acid are added, these solutions keep the pH value as steady as possible. Illustration 4a shows a buffer solution made up of $CH_3COOH/CH_3COONa$ (acetic acid and sodium acetate). The universal indicator in illustrations 4b and 4c shows that the pH of the solution remains constant despite the addition of HCl and NaOH.

4a

4b

4c

# THE EXPERIMENTAL DETERMINATION OF pH

## calculating the hydrogen-ion concentration in a solution

To produce a ...l sour pickle, a food processor must ...ow how much vinegar to use in his p... ...g solution. In a similar manner, a ...ner must be able to determine the ... ...inity of his soil so that adjustments ca... made for proper crop growth. What ...thods can be used to find answers ... the processor and grower? The a... ...ty or alkalinity can be determined fr... ...he hydrogen-ion concentration in a ...ation of the substance.

The negativ... ...garithm of the hydrogen-ion concen... ...tion of an aqueous, or water, solution... ...efined as its pH value. This "quantity" ... convenient expression of a solution's ...dic and basic characteristics:

$$pH = -\log [H^+]. \qquad (1)$$

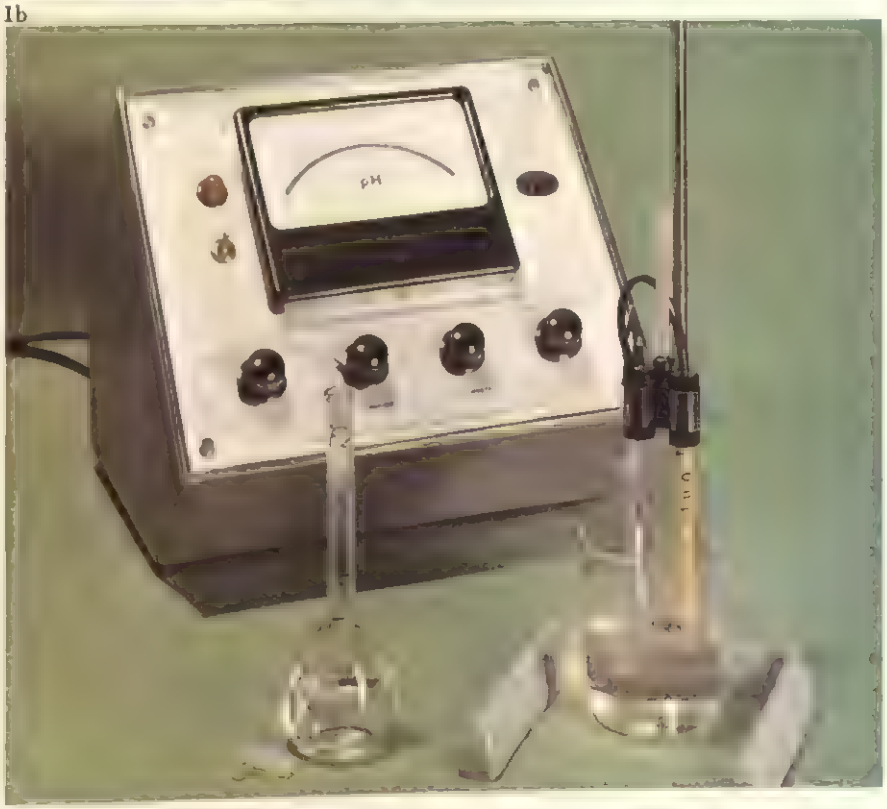
### MEASURING ... WITH INDICATOR...

Indicators ca... ... used to determine a rapid, if not a... ... precise, measurement of the pH va... ...of an aqueous solution. These indicat... ...generally organic compounds—chang... ...olor according to the pH of the solu... ...in which they are dissolved.

The range ov... which an indicator's

1a

1b

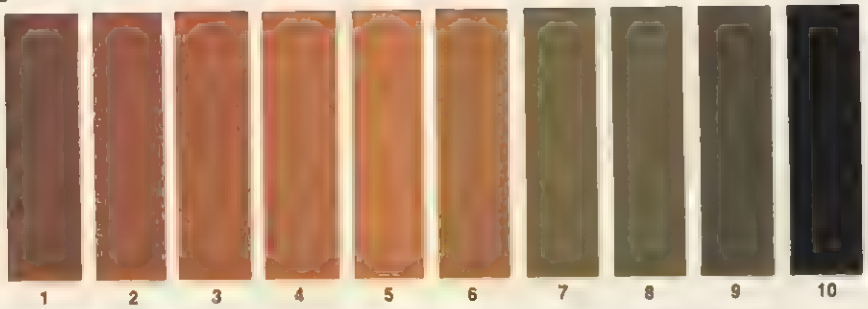


**CALIBRATING THE pH METER AND MEASURING AN UNKNOWN pH VALUE**—Before measuring a solution's pH value with a pH meter, the instrument must be calibrated (illustration 1a). This is done with a solution that adapts the instrument's pH scale to the particular electrode pair being used. The electrodes are first immersed in a solution of known pH (in this case, pH 4). Then, the temperature shown on the thermometer is "set" into the pH meter (second dial from the left) and the meter switched to "measure" (first dial on the right). Finally, an adjustment is made so that the needle points to the known pH value. After calibration in this way, the meter is switched to zero, and the reading of the pH value gives the zero point of the electrode chain (illustration 1b). The meter is now set to measure the pH value of the unknown solution.

color changes, as a function of a solution's pH value, is normally two to three pH units. Therefore, a different indicator must be used according to the range being examined.

To avoid having to use several indicators, a standard mixture showing gradual and continuous color changes over a wide pH range has been developed. This mixture is commonly known as a universal indicator. Illustration 2 shows the changes in color of a universal indicator with variations in pH value from one to ten units.

2




**UNIVERSAL INDICATOR**—The use of indicators permits a quick and convenient method of measuring the approximate value of a solution's pH. Such indicators are generally organic substances that change color according to the pH of the solution in which they are dissolved. Because individual indicators cover only a small pH range, standard, or universal, mixtures have been prepared that are effective through a range of one to ten pH units. The illustration shows how the colors vary as a function of pH value.

To determine the pH value of a solution of unknown hydrogen-ion concentration, a few drops of the appropriate indicator are added to it. The resultant color, when compared to a chart for that indicator, reveals the approximate pH value of the solution. As an alternative a slip of paper saturated with the indicator can be dipped in the test solution. The color of the paper is then compared to the chart to obtain the same result.

## DETERMINING pH WITH A pH METER

Potentiometric methods are the most widely used in determining the precise pH value of a solution. The apparatus used is called a pH meter.

Such equipment, whether simple or complex, is based on the principle of determining the hydrogen-ion concentration in a solution by measuring the difference in potential at the poles of an electrochemical cell. The cell consists of two electrodes: a reference electrode and a measurement electrode. Illustration 4 is a schematic diagram of such a pH meter. The glass measurement-electrode has a very high electrical resistance, on the order of several hundred megohms (one megohm is equal to one million ohms). Accordingly, the potential difference in a cell containing a glass electrode must be measured with a special potentiometer. This electronic voltmeter forms the measuring part of the pH meter.

## PERFORMING A pH MEASUREMENT

Before measuring the pH value of a test solution, the potentiometer, reference electrode, and glass measurement-electrode must be calibrated for accuracy.

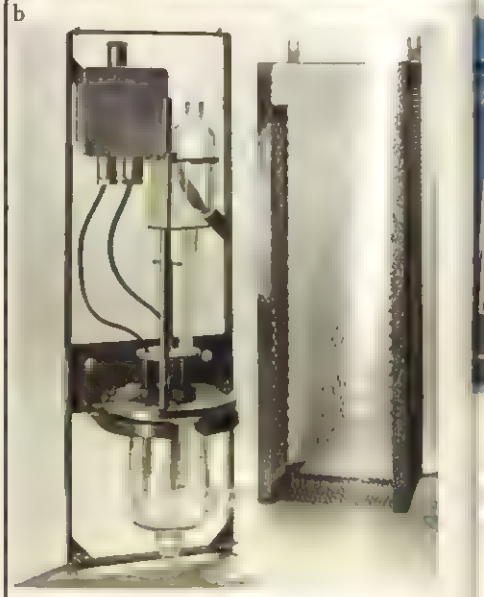
To calibrate the equipment, a number of solutions are used for reference; such solutions with known pH values are available commercially. Using the reference values, the instrument's calibration curve is determined. This provides a true pH value, corresponding to the reading on the instrument. By careful calibration, pH values with an accuracy of one-hundredth of a pH unit can result.

Apart from the high degree of precision they produce, pH meters are quick and easy to use. They can measure solutions having strong oxidizing or reducing properties, and they can be used with very small quantities of liquid.

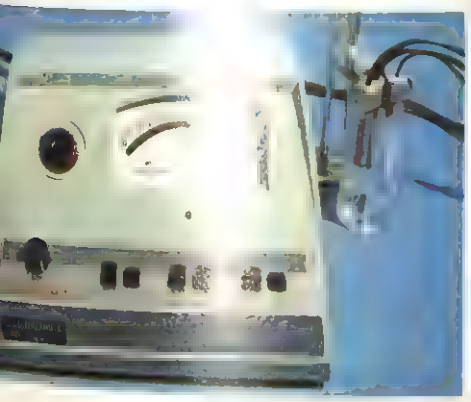
3

a

b

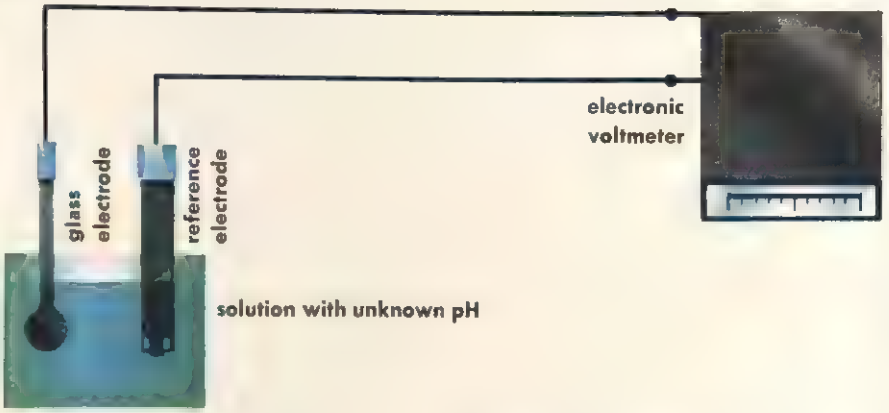


c



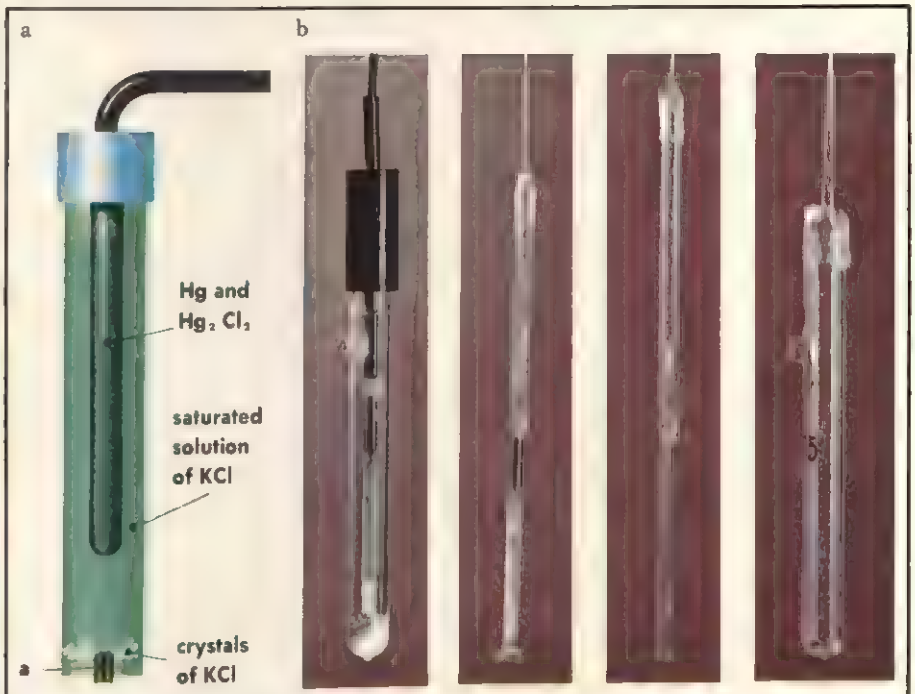
**INDUSTRIAL pH METER**—Illustration 3a shows the inside of an industrial pH meter, with which it is possible to use a pair of electrodes having an electrical resistance as high as 500 megohms. The electrode pair is seen in illustration 3b. In the lower cylinder is a glass (measurement) electrode, a calomel (reference) electrode, and a resistance thermometer. A solution with an unknown pH value is allowed to flow into the cylinder through the inlet at the side, and out through the bottom part. A typical laboratory pH meter is shown in illustration 3c.

4




**pH METER**—This schematic diagram shows how a pH meter works. The measurement and reference electrodes are immersed in the solution having an unknown pH value.

5




**REFERENCE ELECTRODE**—This device gives a constant potential such that, with the potential provided by the measurement electrode, the outside circuit is closed and a potentiometric reading obtained.

A calomel electrode is commonly used in pH meters for reference purposes. Besides having a constant and reproducible potential, this type of electrode is easy to use and manufacture. It is made of metallic mercury (Hg) in contact with calomel ($Hg_2Cl_2$, a slightly soluble salt), and a solution of potassium chloride (KCl). This solution is placed in electrical contact with the solution whose pH value is to be measured. To prevent the two solutions from mixing, a small porous membrane (a) is used for the contact, as in the electrode (illustration 5a).

The potential of a calomel electrode varies according to the temperature and concentration of the potassium chloride solution at equilibrium. When a saturated solution of potassium chloride is used, as is normally the case, the electrode is called a saturated calomel electrode. Illustration 5b shows the various glass components of a calomel electrode.

6

a

**MEASUREMENT ELECTRODE**—In commercial pH meters, a measurement electrode is a glass electrode consisting of a fine bulb of special glass fused to the end of a small-gauge glass tube. The bulb contains a standard solution in which an appropriate electrode is immersed. For example, a silver thread coated with silver chloride can be used as the electrode, and a solution of hydrochloric acid as the standard solution (illustration 6a).

The glass electrode works on the principle that the difference in potential between a glass surface and a solution in contact with it varies regularly as a function of pH. It follows, in this case, that a difference in potential will exist between the inside and outside surfaces of the glass bulb. This difference will change with variations in the pH value of the external solution, while the reference solution inside remains constant. These alterations in potential difference are translated into variable potentials of the electrode immersed in the standard solution according to the relationship:

$$E_{glass} = E^{\circ}_{glass} + 0.0592\ pH. \qquad (2)$$

In this equation, $E_{glass}$ represents the potential of the glass electrode in volts. $E^{\circ}_{glass}$ is the potential that the glass electrode would have if the external pH value were zero. This value clearly depends upon the type of glass chosen, the reference solution used, and so forth. The pH value should be determined for each occasion according to the electrode used. In practice, the relationship (2) between $E_{glass}$ and pH is applicable only for well-defined intervals of hydrogen-ion concentration between two and nine pH units. Generally, it is accurate only to a first approximation. Illustration 6b shows a series of glass electrodes.

b

7

**CHAINS OF ELECTRODES**—Illustration 7 shows two types of electrode pa... Illustration 7a shows a combination glas... and calomel electrode. Shown in illustrati... 7b is a pair of electrodes in a pH meter. ... the left is a calomel reference electrode, a... on the right is a glass measurement-elec... de. The thermometer between the two el... odes is needed to record the exact tem... ture of the test solution during each phase ... the pH measurement.

a

b

# SALT FORMATION | neutralizing an acid with a base

Anyone asked to define "salt" would probably answer "Something used to enhance the flavor of food." And this would be correct. In chemistry, however, table salt is just one member of a large family of compounds known as salts.

The study of salts and their formation is both interesting and vital because man and his environment are dependent on these substances for survival. Examples are penicillin for combating infection and salts of nitrogen, phosphorus, and potassium used in fertilizers to promote plant growth.

An understanding of how salts are formed begins with a look at the reaction between an acid and a base—one of the fundamental concepts in chemistry. When compounds of this type interact, the reaction is called neutralization and two new compounds are formed. These are water, in a relatively large quantity, and a salt. Schematically, neutralization occurs between the $H^+$ ions of the acid and the $OH^-$ ions of the base:

$$H^+ + OH^- \rightarrow H_2O,$$

while salt formation takes place between the base's positive ions (cations) and the acid's negative ions (anions):

$$B^+ + A^- \rightarrow BA.$$

For example, the reaction between hydrochloric acid and sodium hydroxide can be represented in four steps:

$$HCl \rightarrow H^+ + Cl^-$$
$$NaOH \rightarrow Na^+ + OH^-$$
$$H^+ + OH^- \rightarrow H_2O$$
$$Na^+ + Cl^- \rightarrow NaCl$$

(the NaCl is recovered as a solid after evaporation of the water).

If this operation were actually performed, a reasonable comment would be: "Hydrochloric acid (HCl) and sodium hydroxide (NaOH) have been mixed, causing a neutralization reaction and resulting in salt formation. Why can't anything be seen? Where's the salt?"

This is a justified observation. To all appearances there has been no change as a result of mixing the two solutions; however, the sodium chloride (NaCl) formed in the reaction is a salt that dissociates completely in solution. The sodium ions and the chloride ions will move around, independently, surrounded by water molecules. By applying enough external energy to overcome the forces keeping the water in the liquid state, causing the solution to evaporate, the forces of attraction between the $Na^+$ and $Cl^-$ ions will draw these ions closer together as the water molecules evaporate. At this point, the sodium and chloride ions will rearrange themselves according to precise laws and form a crystalline solid. Now, salt crystals will "come out of solution" and be deposited in the container.

Thus, a salt can be defined as a compound derived from the neutralization of an acid with a base. This also explains why salts are so common in nature, while acids and bases are rarely found in the free state. Some extremely weak acids with low levels of reactivity can be found, and boric acid in volcanic steam or hydrogen sulfide in underground natural gases are examples.

## HOW TO PREPARE SALTS

The fundamental reaction in salt formation is neutralization—the result of mixing an acid with a base. There are, however, other methods for obtaining salts. One of these is the action of an anhydride, such as carbon dioxide, on a basic oxide, such as calcium oxide:

$$CO_2 + CaO \rightarrow CaCO_3.$$

The action of an acid on a metal also produces a salt, but only if the metal precedes hydrogen in the electrochemical series of elements (for only then can it displace the acid's hydrogen). Thus, by reacting zinc with sulfuric acid the products are zinc sulfate and hydrogen:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$

A similar reaction using copper in place of zinc would not occur because copper follows hydrogen in the electrochemical series and is unable to displace it. In general terms, this means that elements preceding hydrogen in the series have more energy than hydrogen, and those following hydrogen have less energy. Zinc is, therefore, able to reduce hydrogen and is itself oxidized.

1a

1b

**CARBONATE TESTS**—This reaction, used as an analytic test for the presence of carbonates, is a typical example of salt formation. In illustration 1a, carbon dioxide is a product of the reaction between sulfuric acid and a carbonate (in the lefthand test tube). The liberated gas bubbles into the tube at the right, containing a solution of barium hydroxide, forming barium carbonate:

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O.$$

Barium carbonate is insoluble in water, and collects slowly at the bottom of the test tube (illustration 1b).

2a

2c

2b

2d

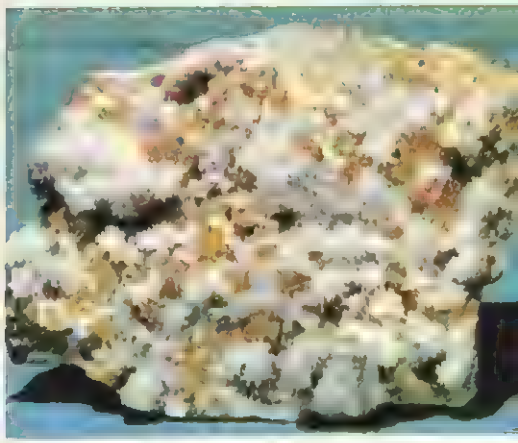
**PRECIPITATION AND FORMATION OF SALTS; CALCITE CRYSTAL**—Illustration 2a shows a simple exchange reaction. Here, $H_2S$ bubbles into a test tube containing a salt of As, with the characteristic formation of yellow $As_2S_3$ as a precipitate. In illustration 2b, sodium chloride is formed according to the reaction $NaOH + HCl \rightarrow NaCl + H_2O$. The white fumes escaping from the beakers in illustration 2c demonstrate that ammonium chloride is being formed in the reaction: $NH_3 + HCl \rightarrow NH_4Cl$. Illustration 2d shows a crystal of calcite ($CaCO_3$) from the island of Elba in the Mediterranean.

3a

3b

3c

3d



**SALTS**—These illustrations show several examples of salts, some of which are found naturally. Illustration 3a is of dolomite ($CaCO_3 \cdot MgCO_3$), found in the Dolomite Mountains of northern Italy. The intense blue of the crystal in illustration 3b identifies it as copper sulfate ($CuSO_4$). A transparent, white crystal of gypsum ($CaSO_4 \cdot 2H_2O$) is shown in illustration 3c, while in illustration 3d are seen crystals of celestite ($SrSO_4$).

3e

3f

The large, characteristically translucent crystal in illustration 3e is alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$). Finally, illustration 3f shows a salt being formed, in this case silver chloride. This compound is formed as the result of a double exchange reaction. Silver chloride is insoluble in water, and its characteristic white flakes cloud the solution.

Copper, however, must first be oxidized before it can be used to form a salt. The reaction of copper and sulfuric acid can be expressed,

$$Cu + H_2SO_4 \rightarrow CuO + SO_2 + H_2O,$$

where the zero valent copper (Cu) has oxidized to $Cu^{++}$. At this stage, salt formation can occur:

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O.$$

This shows how the copper has not carried out any reduction of the hydrogen, but has oxidized at the expense of the sulfur in the sulfuric group. In this case, the acid reacts with the metal's oxide to form a salt, rather than directly on the metal.

Another method of salt preparation involves the reaction of an acid or a base with one salt to produce a different salt. For example, sulfuric acid and sodium nitrate react to form sodium sulfate and nitric acid:

$$H_2SO_4 + 2NaNO_3 \rightarrow Na_2SO_4 + 2HNO_3.$$

This is called a simple exchange reaction because the $NO_3^-$ and $SO_4^{--}$ groups simply change places. In fact, the sulfuric acid displaces the nitric group of the sodium nitrate because of a tendency to form nitric acid, which is less soluble and escapes as a gas. (In other cases, the low solubility of a compound may cause it to precipitate out of solution as a solid.)

Finally, salt may be formed by the double exchange method. This involves an exchange between two salts with different acid and base groups. Thus, sodium chloride and silver nitrate react in solution:

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl.$$

In this case, the silver chloride is much less soluble than the sodium nitrate, and the salt separates from the solution by precipitation. This is generally the case in reactions of this type.

## NEUTRAL, ACID, AND BASIC SALTS

A frequent complaint is "acid stomach," and a common household remedy is bicarbonate of soda. What sort of salt is this, and how does it compare to sodium carbonate? Are these two compounds one and the same? The answer is no; they are quite different from one another and each possesses its own set of chemical properties. Similarly, potassium bisulfate as used in agriculture is distinct from its "cousin," potassium sulfate.

Sulfuric acid, upon dissociation in water, produces $H^+$ and $HSO_4^-$:

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

and the dissociation is complete. For this reason, if a solution containing one mole of $H_2SO_4$ is mixed with a one mole solution of KOH (potassium hydroxide), the H ions neutralize the OH ions. On subsequent evaporation of the solution, one mole of the salt, $KHSO_4$ (potassium bisulfate), remains. If, on the other hand, a two-mole solution of KOH were added to the acid, more protons would be required for neutralization, and a new dissociation would occur:

$$HSO_4^- \rightarrow H^+ + SO_4^-$$

In this case, twice the amount of OH ions would be neutralized. On evaporation, a different salt, $K_2SO_4$ (potassium sulfate), is the product.

However, it must be noted that during dissociation an acid does not give up more than one proton at a time. Accordingly, there are polyvalent acids, such as $H_2SO_4$, that can give up several hydrogen ions depending on the environment. Only when salt formation is complete, with all hydrogen and hydroxyl groups neutralized, is a neutral salt the product of the reaction.

In a situation where hydrogen groups remain available for further neutralization, the reaction products are acid salts. Bisulfate and bicarbonate salts are, in fact, also called acid sulfates and acid carbonates. The term "acid" indicates the presence of an additional hydrogen ion that is available for further reaction. In a like manner, basic salts are those compounds having remaining hydroxyl groups that are able to react further. Bismuth hydrate, $Bi(OH)_3$, when treated with nitric acid, can yield two basic salts and a neutral salt:

$$Bi(OH)_2NO_3;\ Bi(OH)(NO_3)_2;\ Bi(NO_3)_3.$$

Thus, the products of salt formation are everywhere, and salts comprise a large and very important class of chemical compounds. Whether simple or complex, all salts are essentially products of the reaction between acids and bases.

# INDICATORS | deciding when a reaction ends

Two primary methods are used for determining when a chemical titration—whether it is neutralization, precipitation, or reduction—has reached its equivalence point. One of these methods involves the use of high-precision instruments. The other method makes use of indicators. When precision is not so important, the second method is the most convenient and the least expensive.

Indicators are chemical substances that visually indicate the end of a chemical process. They do this by a change of color, by a change in fluorescence, or by the formation of a precipitate. They can be divided conveniently into the following three categories: acid-base indicators, oxidation-reduction indicators, and indicators for precipitation reactions.

## ACID-BASE INDICATORS

Acid-base indicators are used in all neutralization reactions. Such indicators are generally organic substances in which a change of hydrogen-ion concentration or of pH causes alterations in their molecular structure (such as protonation or the breakdown of double bonds), resulting in a change of color in the substance itself.

As a general rule, acid-base indicators are weak acids (or weak bases) that dissociate when immersed in water, according to the equilibrium:

$$HIn + H_2O \rightleftarrows H_3O^+ + In^-.$$

HIn is the acid form of the indicator, while $In^-$ is the basic form. The constant for this equilibrium is:

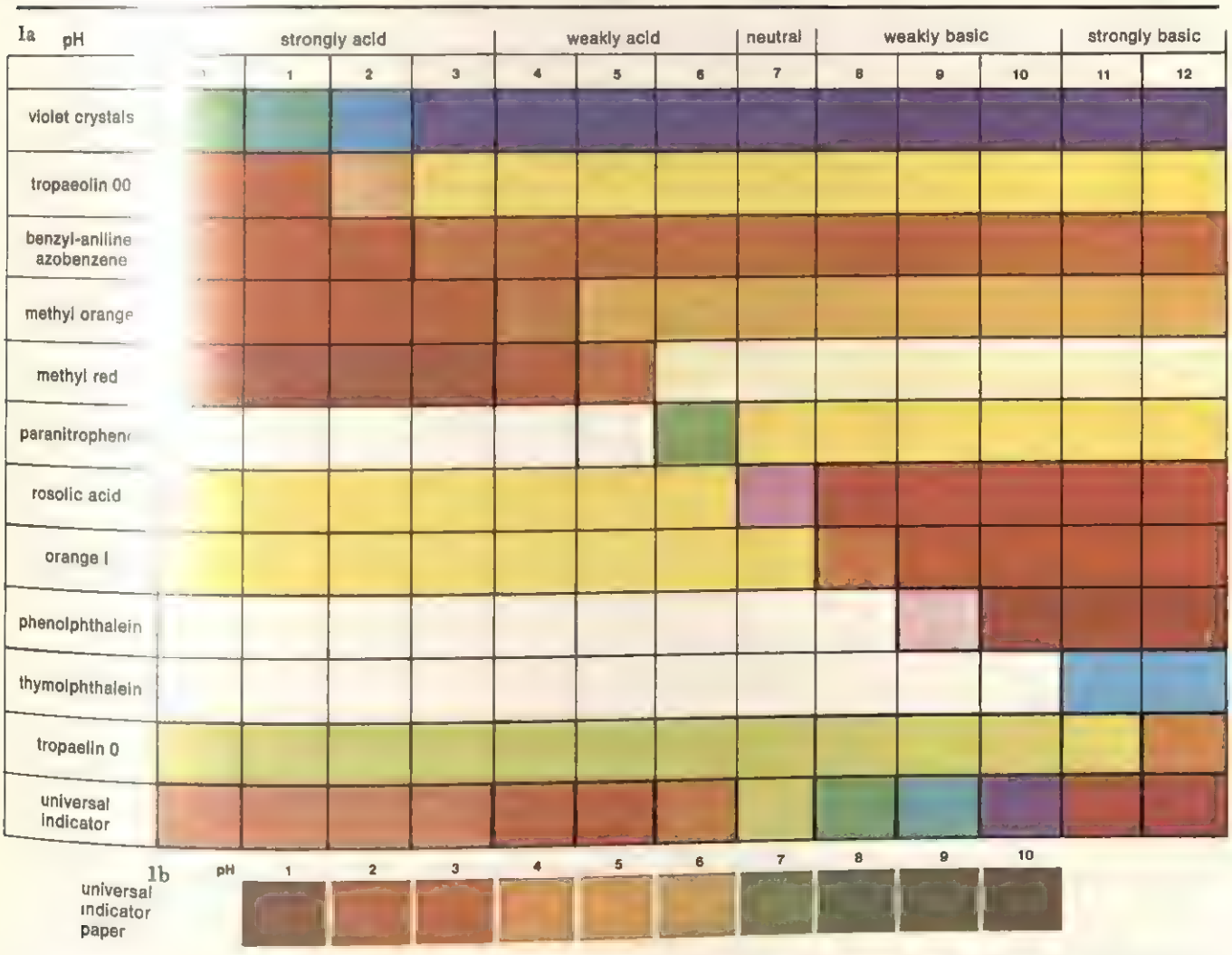
$$K = \frac{[H_3O^+]\,[In^-]}{[HIn]},$$

which gives the equation

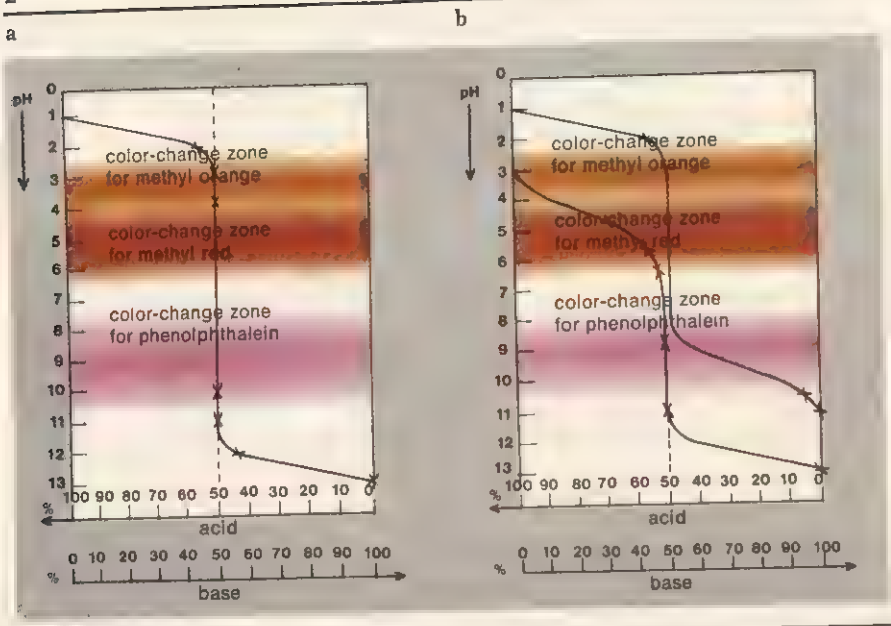
$$\frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{K} \quad . \qquad (1)$$

The addition of acid increases the concentration of hydrogen ions and shifts the equilibrium toward the nondissociated form, which is said to be acid. The addition of a base has the opposite effect, causing an increase in the dissociated form, which is said to be basic. If HIn and $In^-$ are of different colors, it follows that the color of the indicator is directly dependent on the pH of its environment.

When the value of the hydrogen-ion




**AN INDICATOR FOR EVERY pH** — Careful choice of indicators permits the operator to cover the pH range from 0 to 12. Illustration 1a shows the color-change range for some of the more common indicators and their relative color variations. Illustration 1b, at the bottom, shows the colors assumed by a sensitive universal indicator (available commercially) at different pH values.




**TITRATION CURVES**—The graphs shown in this illustration can be used to select the most suitable indicator for a given neutralization reaction. Illustration 2a shows the titration of a strong acid with a strong base. The deduction is that any indicator with a color change range between pH 4 and 10 may be used. Illustration 2b shows two examples. Curve I represents the titration of a weak acid with a strong base (in which the most suitable indicator is phenolphthalein). Curve II represents the titration of a strong acid with a weak base. In this case, because the phenolphthalein would change color only in the presence of an excess of base, the best indicator is methyl red or methyl orange.

concentration is equal to the numerical value of K, then $[In^-] = [HIn]$. The color is halfway between the color for the acid form and the color for the basic form. The numerical value of the corresponding pH is the color-change point of the indicator and is indicated by the letters pK. In practice, an indicator does not change color at an exact pH, but passes gradually from one color to another over a certain range of pH.

The presence of the acid form cannot be detected in a solution containing 90 percent basic form. By increasing the percentage of acid form, a gradual variation of color develops and this may be regarded as virtually concluded when the acid reaches 90 percent.

If the acid form accounts for 90 percent and the basic form for the remaining 10 percent, the result is

$$\frac{[HIn]}{[In^-]} = 10.$$

For equation (1),

$$\frac{[H_3O^+]}{K} = 10,$$

which gives the pH value

$$pH = pK - 1;$$

while if 90 percent is basic and 10 percent is acid, the result is

$$\frac{[HIn]}{[In^-]} = \frac{1}{10};$$

that is,

$$\frac{[H_3O^+]}{K} = \frac{1}{10},$$

hence,

$$pH = pK + 1.$$

The variation of color from one form to the other thus takes place over a range of two pH units. This is known as the color-change range. In special cases it may help to use indicators whose color-change range is quite limited. It is even possible to choose mixtures of indicators with no range at all (with a precise color-change point). Substances can also be mixed to produce universal indicators characterized by continuous color variation for the whole pH range, from 1 to 13. Strips of paper, impregnated with these mixtures, are used commercially. The pH of any solution can be calculated with a fair degree of accuracy by moistening the paper with the solution and observing the resultant color.

It should be remembered that correct use of indicators necessitates keeping other experimental conditions—such as total volume of the solution, solvent, and quantity of indicator—as constant as possible. Only in this way will experimentally reproducible results be achieved. The solvent, in particular, may have an immediate effect on the dissociation of the indicator. A wide variety of these substances, covering a pH range from 2 to 12, is available commercially.

Indicators are generally prepared in a 1-percent water solution, with the choice of indicator made on the basis of the acid-base neutralization curve.

The hydrogen-ion concentration in the titration of strong acids with strong bases nearing the point of neutrality varies greatly, so that any indicator with a color-change range between pH 4 and 10 can be used (the most common indicator is methyl orange). In the titration of a weak acid (such as acetic acid) with a strong base in water, the solution at neutralization point (when the acid-base proportion is equal) will be basic because of the hydrolysis of the salt formed in the solution. The indicator required in this case is phenolphthalein, whose color-change range extends from pH 9 to 10. The point of equivalence for acetic acid (0.1 M—molar concentration) shows a pH variation of from 7 to 10.

In the case of a weak base (such as ammonia), or a strong acid, exactly the opposite happens. At neutralization point, the solution is acid and the indicator required is methyl red, an indicator whose color-change range goes from pH 3 to 6.

## OXIDATION-REDUCTION INDICATORS

Oxidation-reduction indicators are sub-

stances whose color in the oxidated state is different from that in the reduced state. The equilibrium in this case is

$$I_{ox} + ne^- \rightleftarrows I_{red},$$

and the oxidation-potential of the indicator is

$$\epsilon = \epsilon_0 + \frac{.059}{n} \log \frac{[I_{ox}]}{[I_{red}]},$$

where $n$ is the number of electrons involved in the oxidation-reduction process, $I_{ox}$ is the oxidized form of the indicator, and $I_{red}$ the reduced form. An indicator introduced into an oxidation-reduction system sets up the following equilibrium: $S_{ox} + I_{red} \rightleftarrows S_{red} + I_{ox}$.

In practice the indicator takes on the same potential as the system, because of its small concentration. This is indicated by the color it assumes. The color-change point is reached when the concentration of the oxidized form equals that of the reduced form, although here, also, it is a question of the color-change range rather than a precise value. The usual range is around 0.1 volts. If the results are to be accurate, the oxidation-reduction reaction of the indicator must be reversible; otherwise, there is the risk of the color changing before the end point of the titration is reached. This could be caused by a local excess of one of the reagents.

Ferrous iron, for example, can be titrated with cerium (IV) using o-phenanthroline as the indicator. This substance forms a red complex with bivalent iron and a pale blue complex with trivalent iron. The end point of the titration is thus easy to determine.

Some oxidation-reduction reactions do not require an indicator. This happens when one of the reagents itself changes color according to whether it is reduced or oxidized. Such is the case of $KMnO_4$ and $I_2$. The end point of titration in the case of iodine can be brought out even more clearly by adding starch, which gives a deep blue color with iodine.

## INDICATORS FOR PRECIPITATION REACTIONS

Other kinds of indicators work on principles different from those thus far considered. Such indicators are chiefly used

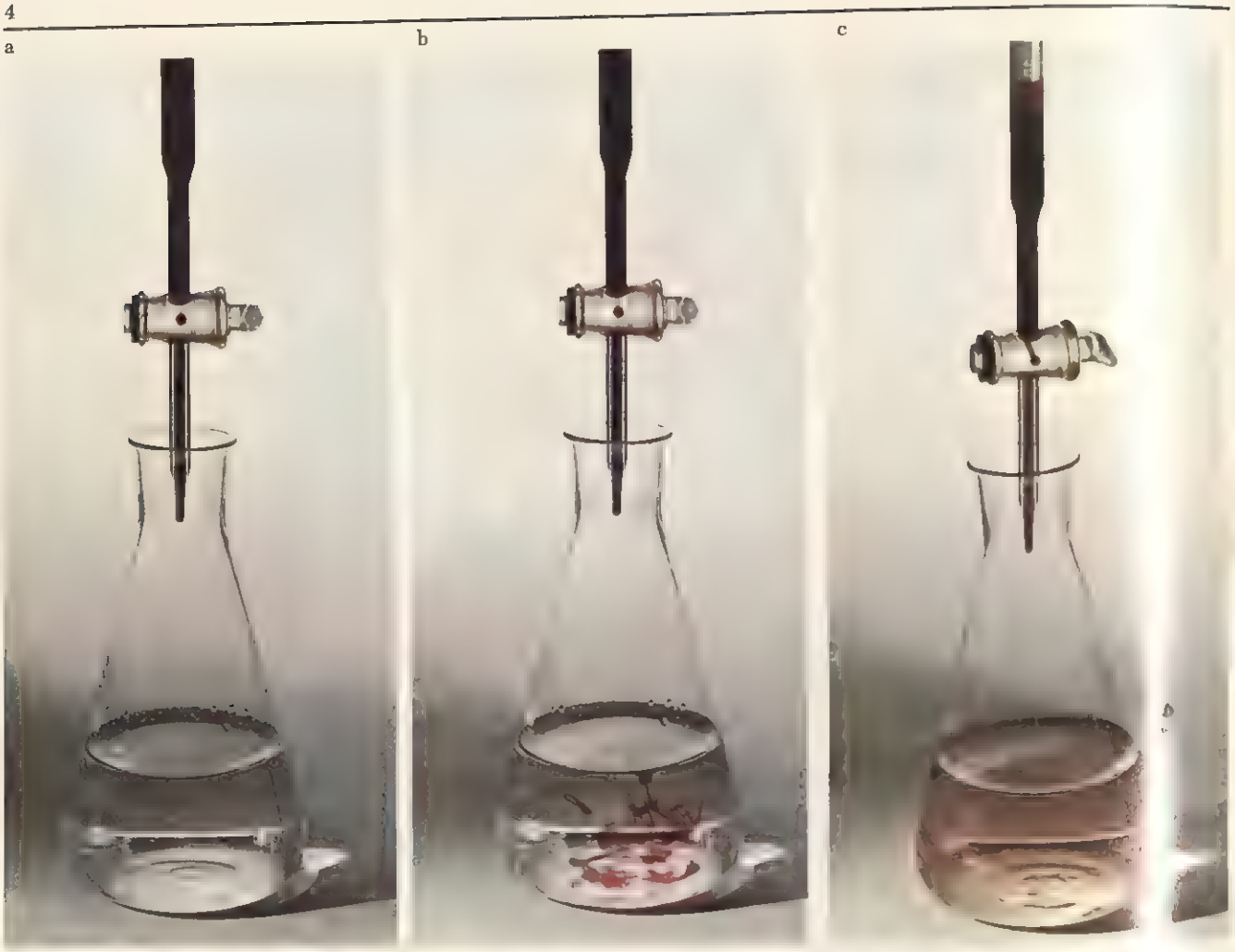


a

b

**TWO COMMON INDICATORS**—Of all acid-base indicators, the ones most used in laboratory work are methyl orange and phenolphthalein. Illustration 3a shows methyl orange (in the graduated cylinder). It turns red in an acid solution (left) and yellow in a basic solution (right). Its color-change range extends from pH 3 to 4, which makes it suitable for use in titrating strong acids with strong bases. Illustration 3b shows phenolphthalein. This is colorless in an acid solution and reddish violet in a basic solution. Its color-change range extends from pH 8 to 10, and it is used in weak acid-strong base titrations.

4




**OXIDATION-REDUCTION TITRATION**—No indicator is required in the case of the titration of oxalic acid with permanganate ($2MnO_4^- + 5(COO^-)_2 + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$). This is because the permanganate ion is a deep violet color, while the manganous ion is a pale pink—so pale as to appear colorless in solution. Illustration 4a shows the sulfuric acid solution of oxalic acid. It is quite colorless. As titration begins (illustration 4b), the first drops of permanganate solution lose their color and the solution remains colorless. During the latter stages (illustration 4c), the permanganate loses its color with increasing difficulty, until the first drop in excess turns the solution pink—marking the equivalence point of the oxidation-reduction process.

to determine the end point of precipitation reactions. The most common of these are the adsorption indicators (which produce soluble colored complexes) and indicators producing colored precipitates.

Adsorption indicators are substances that are adsorbed on the surface of the precipitate, coloring it deeply. A common example is the titration of chlorides with $AgNO_3$ in the presence of fluorescein. In the presence of a small excess of $AgNO_3$ at the end of the precipitation, the precipitate adsorbs the $Ag^-$ ions, which give a pink complex with the fluorescein anions, coloring the precipitate.

Other indicators react with an excess of titrant to produce soluble colored complexes. For example, titration of the silver ion with thiocyanate is done in the presence of ferric alum. The silver ion reacts with the thiocyanate ion to produce a white precipitate of silver thiocyanate. One drop too much causes a reaction with the ferric ions, producing a deep red soluble complex.

Finally, there are the indicators that produce colored precipitates. Titration of a chloride with $AgNO_3$ can also be done in the presence of traces of potassium chromate. When the precipitation of the silver chloride is complete, the excess of silver nitrate reacts with the potassium chromate to form a deep red silver chromate.

In all the cases cited, the indicator must be chosen in such a way that it does not interfere with the main reaction. The equilibriums of the reactions—and the solubility of the various salts—must be considered to enable the choice to fall on an indicator that reacts only when the end point of the titration is reached. In the last processes described above, for example, the silver chromate is much more soluble than the silver chloride; the silver chloride precipitates quantitatively before the precipitation of the chromate can begin.

# ELECTROCHEMISTRY | passage of electric current in solutions

Electrochemist[illegible] he science of chemical reactions [illegible] by electric current, and of reaction[illegible] ead to the development of electri[illegible] rgy. The connection of electrochem[illegible] ith physics is close. Many scientist[illegible] d electrochemistry as a speciali[illegible] nch of physical chemistry.

Electrochemi[illegible] egan toward the end of the eighteen[illegible] ntury with the work of the Italian a[illegible] ist Luigi Galvani in his famous exp[illegible] nts on frogs. Electrochemistry cont[illegible] through the experiments of the [illegible] enth-century Italian physicist Aless[illegible] Volta, and reached its full develo[illegible] through the efforts of an internati[illegible] ay of scientists: the Swedish chem[illegible] nte Arrhenius, the German physi[illegible] mist Walter Nernst, the Dutch phy[illegible] emist Jacobus Van't Hoff, and the [illegible] ssian-German physical chemist Friedr[illegible] Ostwald.

## ELECTROCH[illegible] CAL CELLS

All solid or [illegible] id substances can be conveniently p[illegible] into one of two categories, depend[illegible] whether or not they are good cond[illegible] of electric current: conductors, or [illegible] onductors. Conductors can be fu[illegible] classified into electronic conducto[illegible] electrolytic conductors, according [illegible] the way in which conduction tak[illegible] place.

Electronic co[illegible] ctors, which include metals, are thos[illegible] in which conduction takes place as a result of a flow of electrons (the electric current). Because the mass of the electrons is completely negligible, the passage of the electric current is not accompanied by the appreciable transference of matter. In electrolytic conductors (a solution of sodium chloride in water, for example), conduction takes place because electrolytes in solution dissociate into ions (atoms or groups of atoms that are electrically charged). The term ion comes from the Greek and means "going"; positive ions are called cations, and negative ions are called anions. These particles, being electrically charged and present in a fluid medium, can move in the presence of an electric field, causing a transference of charge accompanied simultaneously by a transference of matter. Processes such as these are made to occur in so-called electrochemical cells.

An electrochemical cell consists of a container in which the relative electrolyte solution and two suitable metal conductors called electrodes are held. The electrode connected to the negative pole of the source of electromotive force (for example, a cell or a storage battery) is called the cathode because the cations, or positively charged ions, move toward it; the electrode connected with the posi-

**ION FORMATION**—Positive ions (cations) are those that have lost one or more electrons. Negative ions (anions) are those that have acquired one or more electrons in relation to the valences of their relative metals.

1

positive ions (cations)

$Ag \rightarrow Ag^{+} + 1e^{-}$
$Zn \rightarrow Zn^{2+} + 2e^{-}$
$Pb \rightarrow Pb^{2+} + 2e^{-}$
$Al \rightarrow Al^{3+} + 3e^{-}$

negative ions (anions)

$Cl + 1e^{-} \rightarrow Cl^{-}$
$Br + 1e^{-} \rightarrow Br^{-}$
$I + 1e^{-} \rightarrow I^{-}$
$S + 2e^{-} \rightarrow S^{2-}$

2

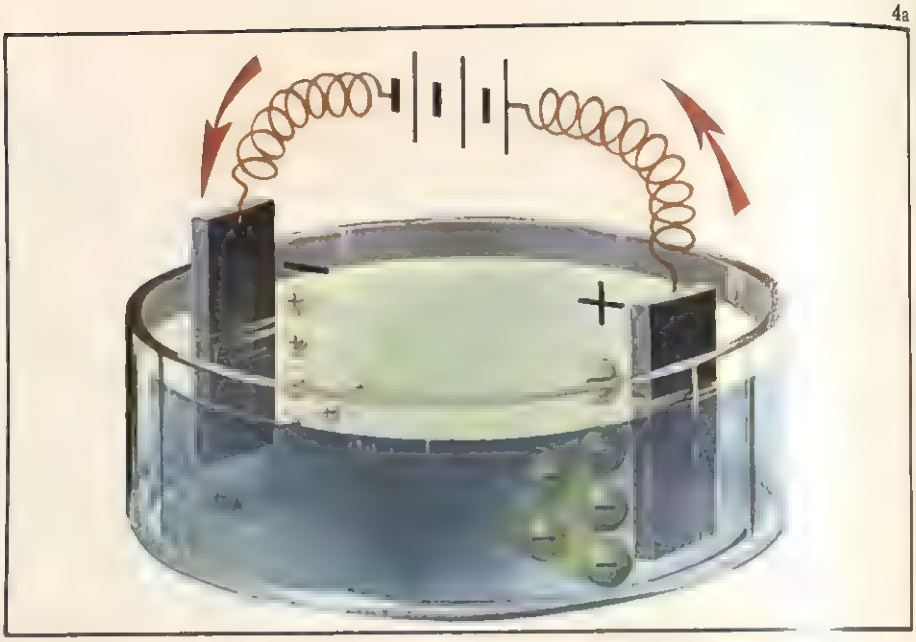
**ELECTROLYTIC CELL**—The electrolytic cell shown in the illustration consists of a silver crucible acting as the cathode; the anode, also silver, is suspended in a solution of silver nitrate, $AgNO_3$. When the two electrodes are connected to the poles of a battery and electric current is passed through, the silver ions of the anode pass into solution, are deposited on the walls of the crucible, and revert to metallic silver.

3a

**SILVER ANODE AND CATHODE**—The most important parts of an electrolytic cell are the anode and the cathode. The anode (illustration 3a) consists of a piece of metallic silver connected to the positive pole of the cell. As current is passed through, the silver is gradually used up, passing into solution. The cathode (illustration 3b) is connected to the negative pole of the cell. The tiny beadlike substance clinging to the walls of the crucible is metallic silver that has passed out of solution and has been deposited on the cathode.

3b

4a



**ANOTHER ELECTROLYTIC CELL**—This cell (illustration 4a) consists of two silver electrodes (two plates, for example) connected to a source of electromotive force and immersed in a water solution of silver nitrate. This salt is dissociated in water solution into $Ag^+$ and $NO_3^-$ ions. When electric current is passed through the cell, several things happen: (1) The positive ions ($Ag^+$) in the solution are attracted toward the cathode, and the negative ions ($NO_3^-$) toward the anode. (2) When the $Ag^+$ ions reach the cathode, they find it rich in electrons because it is connected to the negative pole of the source of electromotive force, and thus cause the reaction

$$Ag^+ + e^- \rightarrow Ag$$

where $e^-$ is the electron. The result of this is a deposit of metallic silver on the electrode. If the electrode is a plate, it will now be noticeably thicker (illustration 4b). (3) While this is happening, the $NO_3^-$ ions reach the anode and find it deficient in electrons because it is connected to the positive pole of the source of electromotive force, and thus cause the reaction

$$NO_3^- \rightarrow NO_3 + e^-,$$

followed by another

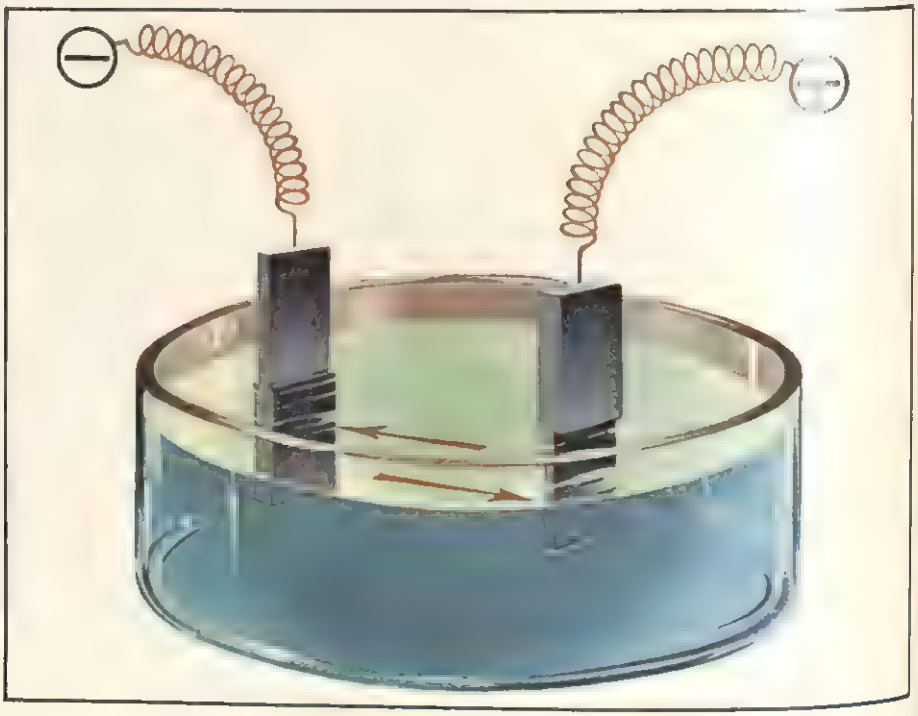
$$Ag \rightarrow Ag^+ + e^-,$$

the overall result being

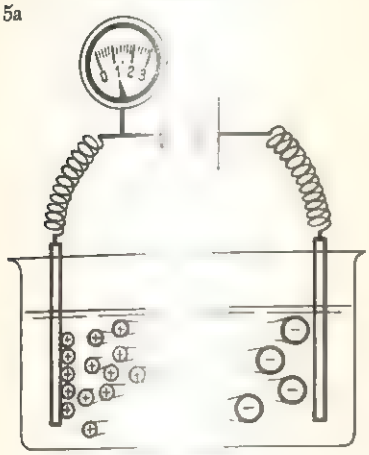
$$NO_3 + Ag \rightarrow NO_3^- + Ag^+.$$

In other words, an atom of neutral silver from the electrode passes into solution in the form of a positive ion, at the same time surrendering an electron to the electrode. The result is that the plate of silver that constitutes the anode is progressively thinned down (illustration 3b). The result of this entire electrochemical process is that the passage of electric current through the cell has caused a transference of metallic silver from the anode to the cathode, and at the same time a passage of electrons from the cathode to the anode in the external electrical circuit. The concentration of the solution does not vary because one atom of silver passes into solution for every atom of silver that is deposited.

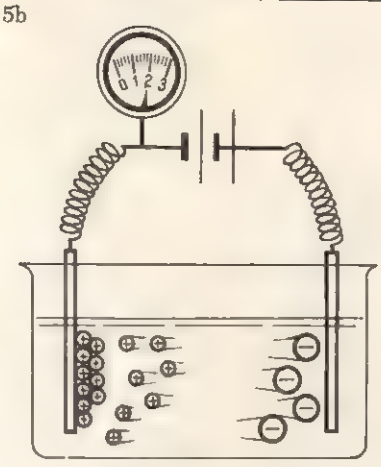
4b



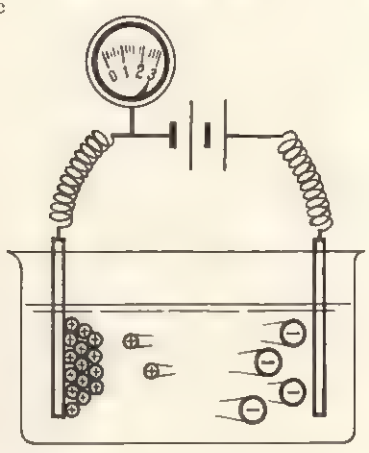
5a



5b



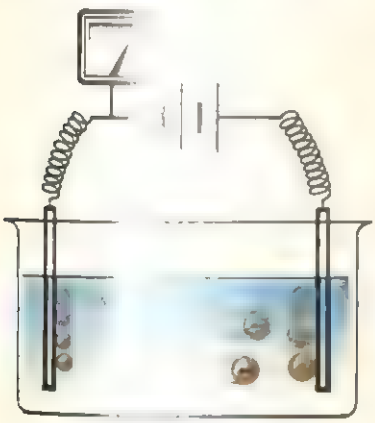
5c



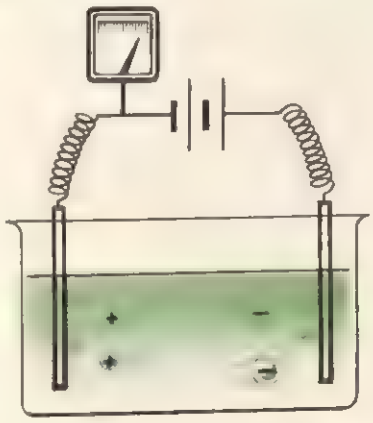
**THE FIRST LAW** ARADAY—The quantity of electricity tha ses through a solution is proportional quantity of substance decomposed. One coulomb of electricity deposits 1.118 mg of silver on the cathode (Illustration 5a); two coulombs double that quantity (illustration 5b); three coulombs triple it (illustration 5c).

**THE SECOND LA** F FARADAY—The same quantity of electr deposits different quantities of metal, nding on the equivalent weight of the m Illustration 6a shows a solution containing salts of $Cu^{2+}$; illustration 6b a solution of salts of $Mg^{2+}$; and illustration 6c a solution of salts of $Zn^{2+}$. The quantity of each metal deposited is represented by the number of spheres shown, varying from element to element in proportion to the equivalent weight of each metal.

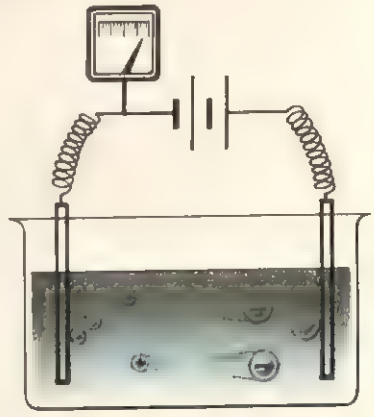
6a



6b



6c



tive pole is called the anode because the anions, or negatively charged ions, move toward it.

## FARADAY'S LAWS

When an electric current is passed through an electrolyte solution, matter is transferred and can be deposited on the electrodes.

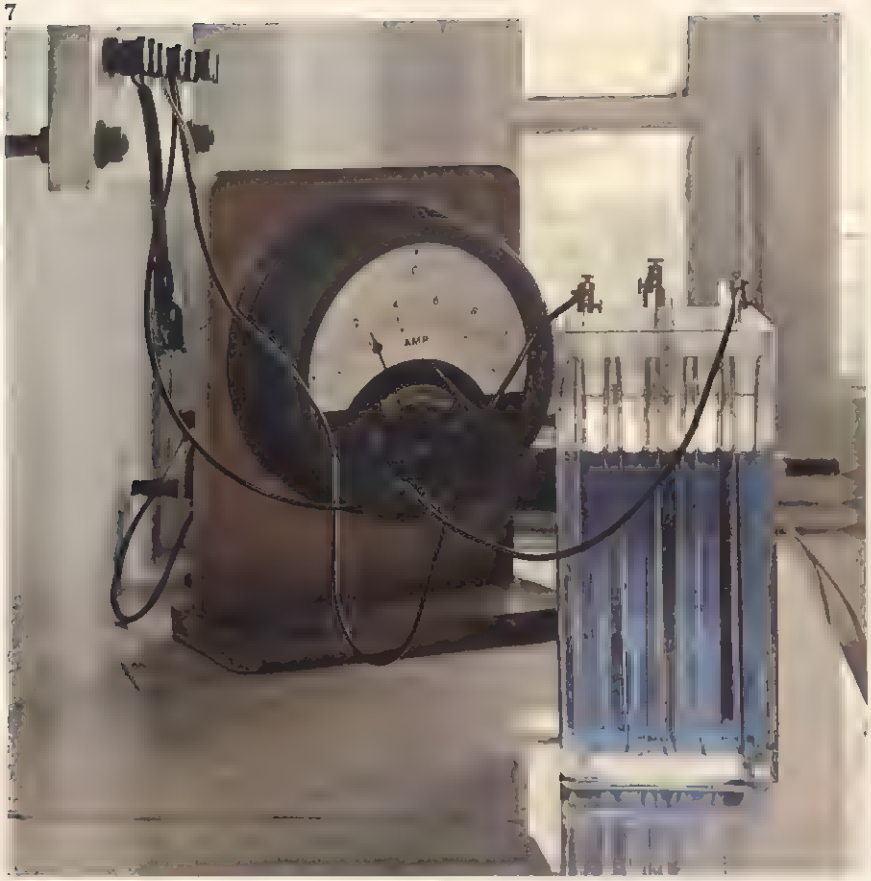
The English physicist and chemist Michael Faraday carried out a series of important experiments on conduction through electrolytes, leading to the formulation of his two famous laws in 1833–1835. These laws describe the relation between the quantity of current passed through an electrochemical cell and the quantity of matter deposited or dissolved on the electrodes.

Faraday's first law states that the quantity of substance decomposed by the electric current is proportional to the quantity of current passed through the solution. In practice, this means that an increase in current increases the amount of metal deposited on the cathode, and the proportion between the two is direct (see Illustration 5). The unit of quantity of electricity used is generally the coulomb, which is the quantity of electricity required to deposit 1.11800 mg of silver on the cathode of an electrochemical cell (the time factor is immaterial).

Faraday's second law states that an equal quantity of electricity decomposes quantities of different substances that are proportional to their respective equivalent weights. Application of this law requires an understanding of the meaning of equivalent weight.

The equivalent weight of a metal is obtained by dividing its atomic weight (the weight of $6.023 \times 10^{23}$ atoms—one mole—of that metal, expressed in grams) by its valence (the number of charges contained in the ion of the metal). Silver, for example, has an atomic weight of 107.88 and a valence of 1, and thus has an equivalent weight of 107.88 g. Zinc has an atomic weight of 65.38 and a va-

7



**COPPER SULFATE VOLTAMETER**—The tank shown contains a blue solution of copper sulfate ($CuSO_4$) and three electrodes of metallic copper, two of which act as cathodes and one (center) as an anode. These electrodes are connected to the corresponding poles of a battery. The ammeter shows current variations.

lence of 2, and thus has an equivalent weight of 32.69 g.

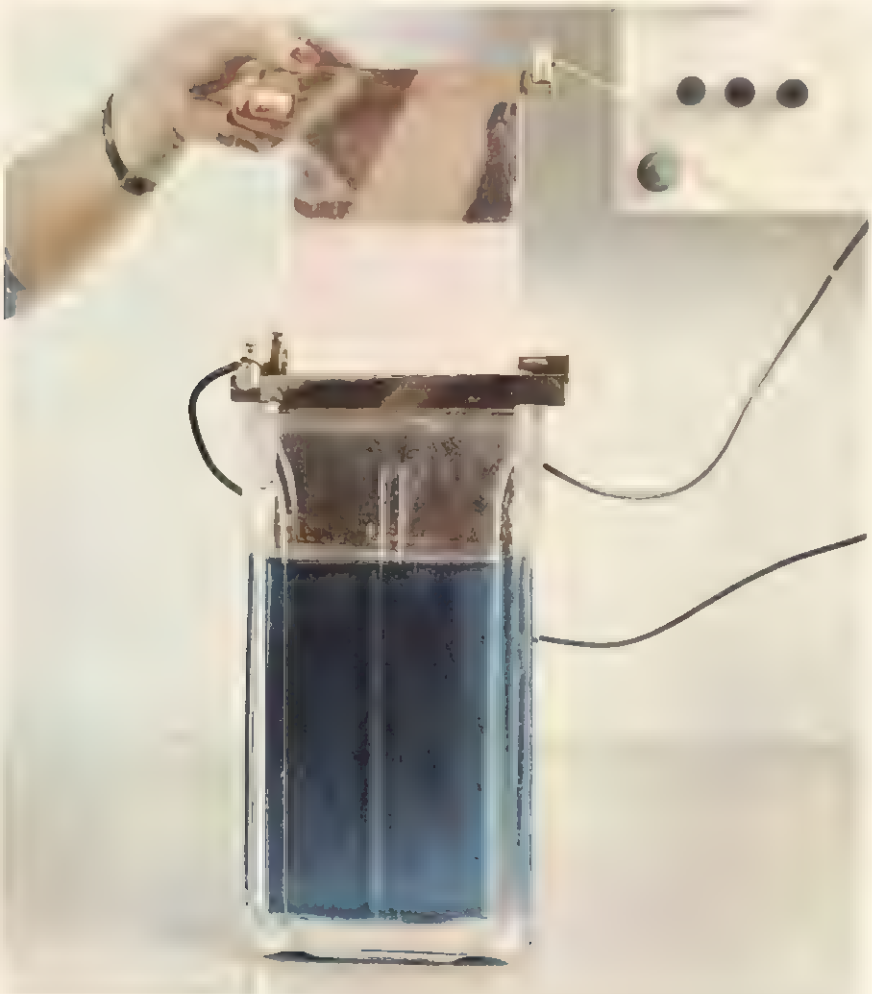
In practice, Faraday's second law means that an equal quantity of current deposits different weights of metal on the electrodes of a cell if different metals are used. The weight of metal deposited by a given current depends on the equivalent weight of the metal.

The law also makes it possible to calculate the quantity of current required to deposit an equivalent weight of a given substance on the electrode. Given that 1 coulomb deposits 1.11800 mg of silver, the equivalent weight of silver (107.88 g) will be deposited by

$$\frac{107.88}{0.00111800} = 96{,}493 \text{ coulombs}$$

This quantity of charge, normally rounded off to 96,500, is known as a faraday in honor of the English scientist Michael Faraday. A faraday is, therefore, the quantity of charge required to deposit (or generate) on the electrodes of a cell the quantity of substance corresponding to its equivalent weight.

8



## INDUSTRIAL APPLICATIONS OF ELECTRODEPOSITION

Several practical possibilities result from studying electrolytic conductivity, and techniques for depositing metals by electrochemistry or electrodeposition are quite common. Electrodeposition is the basic process involved in electroplating and galvanoplasty. Electroplating involves covering an object made of some base metal with a layer of noble metal, either for aesthetic reasons or for protection. Examples of this are chromium-plating, silver-plating, and gold-plating. Galvanoplasty, on the other hand, involves making a cast or mold of an object in a material such as plastic and then reproducing the object in metal. The mold is made conductive by including a layer of graphite, for example; the graphite is inserted into an electrolytic cell as the cathode and is plated with the metal.

**THE USE OF ELECTRODES**—This illustration shows the same tank pictured in illustration 7. One copper electrode has been taken out of the tank to show the sharp dividing line between the part that was immersed, and on which more metallic copper has been deposited, and the part that remained above the level of the solution.

# ELECTROCHEMICAL CELLS

## simple devices for generating electric current

Previous articles ...ated electrochemical cells and the law... Faraday, which govern the passa... of electric current through solutio... An elementary analysis of the chem... effects produced by the passage of ...ric current through an electrochemi... ell has also been presented. Wheth... or practical or academic purpose... e methods used to generate elect... current in devices called electroc... al cells are worth studying. Befor... detailed description of the more impor... electrochemical cells is presented, ho...er, it is necessary to describe the b... characteristics of all such cells.

### BASIC CHARA... ERISTICS OF AN ELECTRO... EMICAL CELL

An electrochem... cell is any device that transforms che... al energy into electrical energy... are two types of cells: primary... which last only until the chemical ... has been exhausted (examples are ... for flashlights, transistor radios, c... s, and so forth); and secondary, or ... ge cells, which can be recharged ... pplying an external source of curre... A storage cell, as the name implies, ... designed to store energy until it is ...ded. The automobile battery is a sto... e cell. Storage cells are described in the ...xt article. This article will discuss primary cells.

A cell requires a container and is sometimes divided into two parts by a special porous membrane. Cells contain a solution, or two different solutions, in which electrodes are suspended. The porous membrane keeps the two solutions separate and at the same time maintains electrical contact.

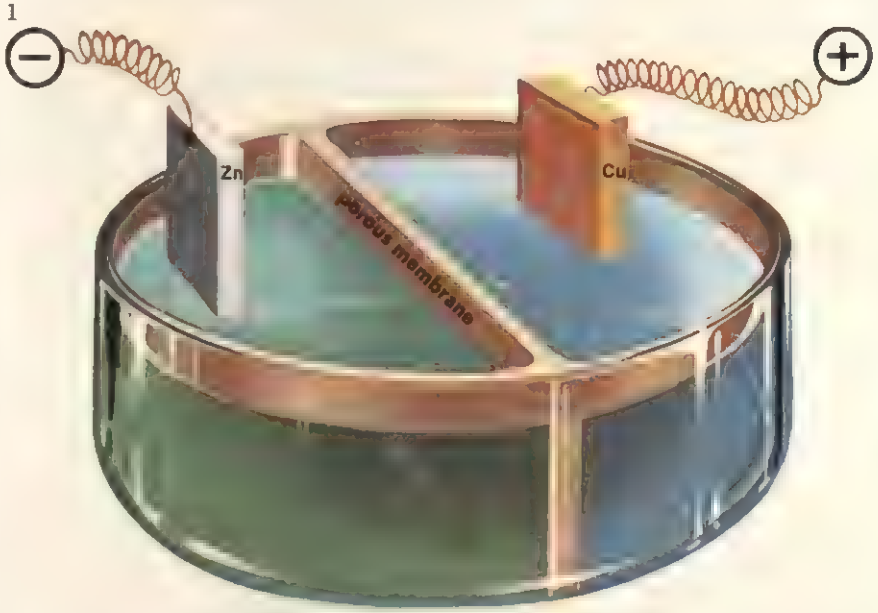
### DANIELL CELL

The Daniell cell provides a clear picture of how electrochemical cells work. This type of cell consists of two solutions: an aqueous solution of zinc sulfate containing a zinc electrode, and an aqueous solution of copper(II) sulfate containing a copper electrode. The two solutions are separated by a porous porcelain membrane (Illustration 1). The cell works as follows: copper metal is deposited on the copper electrode while an equivalent amount of zinc passes into solution. To be more precise, metallic zinc goes into solution as zinc ions and copper ions are plated out as the metal on the copper electrode. The overall reaction is:

$$Zn\,(\text{electrode}) + Cu^{2+}\,(\text{solution}) \rightarrow Zn^{2+}\,(\text{solution}) + Cu\,(\text{electrode}). \quad (1)$$

This reaction is the sum of the two reac-

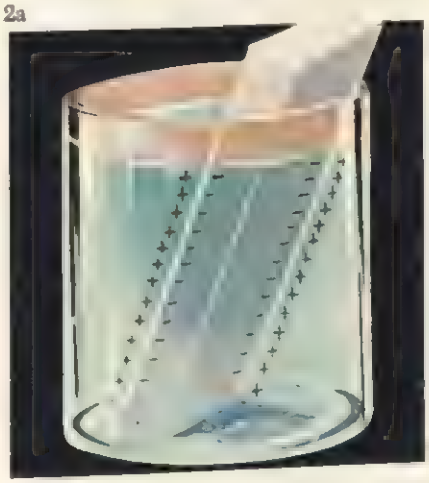
1




**THE DANIELL CELL**—This cell consists of an aqueous solution of zinc sulfate containing a zinc electrode, and an aqueous solution of copper(II) sulfate containing a copper electrode. The two solutions are separated by a porous porcelain membrane. The zinc electrode (the cathode) is negatively charged and thus rich in electrons. The copper electrode (the anode) is positively charged and is deficient in electrons.

**CHARGES**—Zinc (Illustration 2a) passes into solution as $Zn^{2+}$ ions, leaving an excess of electrons on the electrode, which becomes negative. Copper metal, on the other hand, plates out on the other electrode (Illustration 2b), which becomes positive.

2a



2b

tions taking place at the individual electrodes. The reaction at the zinc electrode is (Illustration 2a):

$$Zn \longrightarrow Zn^{2+} + 2e^{-}. \qquad (2a)$$

As zinc atoms leave the electrode and go into solution as $Zn^{2+}$ ions, electrons ($e^{-}$) are left behind on the electrode. The reaction at the copper electrode, on the other hand, is (Illustration 2b):

$$Cu^{2+} + 2e^{-} \longrightarrow Cu^{0}. \qquad (2b)$$

This reaction, however, results in an excess of positive charge at the copper electrode. The sum of reactions (2a) and (2b) gives the overall reaction (1).

These reactions can only take place if electrons are transferred from the zinc electrode to the copper electrode. This is what happens when the electrodes are connected by means of an external conductor such as a piece of wire. Reaction (1) occurs at the same time that a flow of electrons passes through the conductor from the zinc electrode to the copper electrode. This external flow of electrons is the electric current generated by the cell.

A cell of this type is rather short-lived. For the cell to work, reaction (1) must take place, but this means using up the metallic zinc electrode and the copper ions of the copper(II) sulfate solution. As soon as either the metallic zinc or the $Cu^{2+}$ ions are used up, reaction (1) stops and the flow of electrons in the external circuit stops.

Finally, the electrode rich in electrons (the zinc electrode) takes on a negative charge, while the electrode deficient in electrons (the copper electrode) takes on a positive charge.

The conventional method of describing electrochemical cells is to write out the sequence of chemical events that take place, starting at the negative electrode. In this manner, the Daniell cell, which consists essentially of a zinc electrode, an aqueous solution of $ZnSO_4$, a porous membrane, an aqueous solution of $CuSO_4$, and a copper electrode, is described as:

$$Zn/ZnSO_4\ (sol.) \parallel CuSO_4\ (sol.)/Cu.$$

The double bar indicates a separation in the cell. The electromotive force (emf) generated by the cell described above at approximately 25° C (77° F) is shown by the equation

$$E = E^{\circ} - 0.0296 \log \frac{C_{Zn^{2+}}\ (25^{\circ}\,C)}{C_{Cu^{2+}}} \qquad (3)$$

where $E^{\circ}$ is a constant (the standard potential) of the cell. $E^{\circ}$ is the electromotive force supplied by a Daniell cell of the type described above when the concentrations of zinc ions ($C_{Zn^{2+}}$) and copper ions ($C_{Cu^{2+}}$) are both equal to 1. Assuming $C_{Zn^{2+}} = C_{Cu^{2+}} = 1$, and given that $\log 1 = 0$, equation (3) gives

$$E = E^{\circ} - 0.0296 \log 1 = E^{\circ}.$$

The electromotive force of a cell varies with temperature. At 25° C (77° F) the value of $E^{\circ}$ for the Daniell cell is about 1.10 V (volts).

3a

3b

**THE PARTS OF A DANIELL CELL**—Illustration 3a shows an assembled Daniell cell. The individual parts are shown in Illustration 3b: copper anode (left), porous membrane, zinc cathode, glass container with $ZnSO_4$ solution. The copper anode is immersed in $CuSO_4$ solution inside the porous cup.

4

**WARNING LIGHT**—When the electrodes of a cell are connected by a conductor, electrons flow from the cathode to the anode. This flow of electrons is the electric current, which causes the bulb filament to light.

5

**VOLTA'S PILE**—An early cell, mentioned here for historical reasons, consists of a vertical series of alternating zinc dishes, pieces of felt soaked in sulfuric acid solution, and copper dishes. The cell is both short-lived and inefficient, largely because hydrogen collects on the electrodes and produces electromotive forces opposed to those generated by the cell itself; as a result, the internal resistance of the cell increases. Cells developed since Volta's time have almost always contained depolarizing substances such as manganese dioxide to prevent the buildup of hydrogen.

**THE SO-CALLED DRY CELL**—This is a modern version of the old dry cell. Introduced into the United States in 1890, dry cells are still used, although the term "dry cell" is misleading. The insides of these cells are actually quite moist. Commercial versions of the dry cell (the photograph shows one taken apart) consist of an outer casing of zinc (the negative electrode), and a graphite rod surrounded by manganese dioxide and granulated carbon. The rod is the positive electrode. The cell is held together by a tightly stretched fabric. A solution of ammonium chloride and zinc chloride, often gelatinized with special substances, occupies the space between the cloth covering and the zinc electrode. Finally, the top of the cell is covered with pitch to prevent drying. The electromotive force produced by this type of cell is between 1.5 and 1.6 V. Economical to produce, these cells do their job reasonably well.

6

7

**MERCURY CELL OR RUBEN-MALLORY CELL**—Widely used in recent years in a variety of commercial applications, the negative electrode of such a cell (illustration 7a) is always zinc; the other electrode is mercury. The electrolyte is an aqueous solution of $K_2CO_3$ (40 percent) in the presence of solid HgO and $Zn(OH)_2$. The parts of a mercury cell are shown in illustration 7b. Mercury cells are quite efficient for their size. They are used chiefly in portable applications where a constant voltage is required. The voltage generated is exactly 1.35 V.

a

b

**NEW KINDS OF CELLS**—Years of research on electrochemical cells have borne fruit in the form of fuel cells in which electricity is produced directly by the reaction of a gas or liquid fuel supplied to one electrode and oxygen or air supplied to the other. The chemicals that react are not sealed within the cell but are supplied to it, as are fuels supplied to internal combustion engines. Fuel cells using liquid hydrogen and oxygen produced electrical power for the Gemini and Apollo space vehicles.

The nuclear reactor illustrated here represents another, more efficient way of transferring energy from chemical reaction to electrical power. Heat energy from the fission reaction taking place within the reactor core is used to convert water to steam. The steam drives a turbine, which drives a generator, which produces electricity.

The neutron-absorbing control rods, shown here with their positioning mechanism, are raised or lowered to maintain the fission reaction at a desired level.

# STORAGE BATTERIES | canned power

These devices, sometimes called accumulators, storage cells or secondary cells, are electrochemical cells capable of converting electrical energy into chemical energy (the charging process). They then store the chemical energy, and yield it on demand in the form of electrical energy (the discharging process). In other words, they act as a storehouse of electrical energy which can then be used in an external circuit as required. For all practical purposes, there are two types of storage batteries that are useful for this task—the lead-acid storage battery and the nickel-iron alkaline battery.

## LEAD-ACID STORAGE BATTERIES

First developed in rather primitive form in 1859, modified and improved versions of the lead-acid storage battery are still in use today.

During the discharge phase, when chemical energy is converted into electrical energy, the battery consists chiefly of a negative electrode made of spongy lead and a positive electrode made of spongy lead mixed with lead(IV) oxide ($PbO_2$). Both electrodes are suspended in a dilute sulfuric acid ($H_2SO_4$) solution having a specific gravity of about 1.25. This solution causes the electrodes to be partially covered with lead(II) sulfate ($PbSO_4$). The description of a lead-acid storage battery system is therefore as follows (the polarity refers to the discharge phase):

$$\mathrm{Pb} \mid \mathrm{PbSO_4} \mid \underset{\text{(dilute)}}{\mathrm{H_2SO_4}} \mid \mathrm{PbSO_4} \mid \mathrm{PbO_2}+. \quad (1)$$

The actual chemical reactions of this type of battery are shown in the following equations. The overall reaction for the discharging process is

$$\mathrm{Pb} + \mathrm{PbO_2} + 2\mathrm{H_2SO_4} \longrightarrow \mathrm{PbSO_4} + 2\mathrm{H_2O}. \quad (2)$$

In this reaction the electrodes are progressively sulfated as the sulfuric acid is used up. Therefore, the initial concentration of sulfuric acid solution, and also its specific gravity, gradually decrease (Illustration 1).

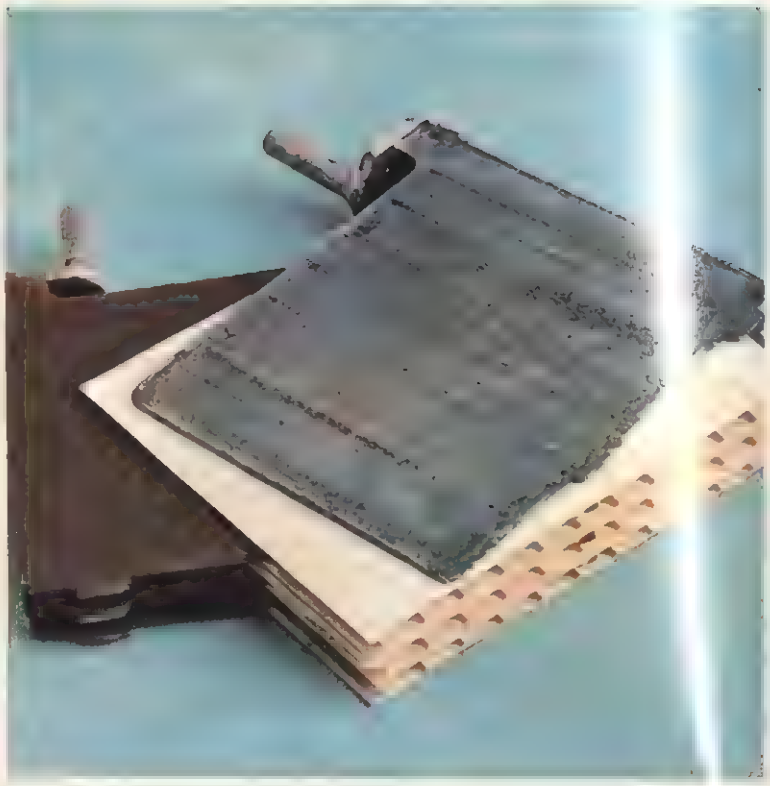
1a

1b

**LEAD ACCUMULATORS** — Storage batteries act as storehouses of electrical energy, and provide a supply that can be drawn on as needed. The lead-acid storage battery was first developed in 1859. Modified and improved versions are still in use today. Illustration 1a shows a lead-accumulator battery normally used to start engines. Illustration 1b, on the other hand, shows a stationary lead accumulator housed in a container of synthetic resin. This battery will supply a current of 200 amperes for short periods of time.

2a

2b



**STARTER BATTERIES**—Illustration 2a shows a large accumulator battery used to start trucks. The positive and negative plates used in this type of battery are shown in illustration 2b. Accumulators convert electrical energy into chemical energy.

The reaction for the charging process, in which external electrical energy is converted into internal chemical energy, is:

$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2H_2SO_4. \quad (3)$$

This is simply the reverse of reaction (2). The electrodes return to their former composition, and the sulfuric acid is regenerated. Charging, therefore, produces a gradual increase in the sulfuric acid concentration and an increase in solution specific gravity to about 1.25. (For the reactions at the electrodes see Illustration 3.)

The complete reaction cycle of a lead-acid storage battery is as follows:

$$Pb + PbO_2 + 2H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O. \quad (4)$$

Since the level of charge on a storage battery is related to sulfuric acid concentration, the specific gravity of the $H_2SO_4$ solution is a measure of the operational condition of a battery. This is why some batteries include a small transparent chamber containing colored balls. The balls rise or fall in the solution in terms of its specific gravity, providing an indication of the level of charge on the battery.

The potential difference of a lead-acid storage battery is thus related to the concentration of the sulfuric acid solution and to its specific gravity. At 25° C (77° F) the potential difference E (expressed in volts) is given by the empirical equation:

$$E = 1.85 + 0.92\,(d-1) \quad (5)$$

where d is the specific gravity of the sulfuric acid solution.

When $d = 1.25$, this formula gives $E = 2.08$ V (volts). Thus, a charged battery at room temperature with its electrolyte at normal concentration supplies a potential difference of 2.1 to 2.2 V. The potential difference increases with increase in temperature at a rate of about 0.0004 V per degree.

It is good practice not to discharge a battery below the 1.8 V level. At this point the $PbSO_4$ grains on the electrodes begin to swell excessively (this is called sulfation of the battery) and interfere with the charging process. It is also good practice not to leave a battery idle for long periods of time, especially when it is already partially discharged. This also can lead to sulfation.

The capacity of a battery is given by the quantity of energy (in terms of electric current supplied for a given time, for example) it is capable of storing. Its yield, on the other hand, is given by the ratio between the quantity of electricity supplied during discharge and the quantity of electricity absorbed during charge. If a battery is working well, its yield may be as high as 90 percent. The average working life of a lead accumulator can be as much as 10 to 14 years.

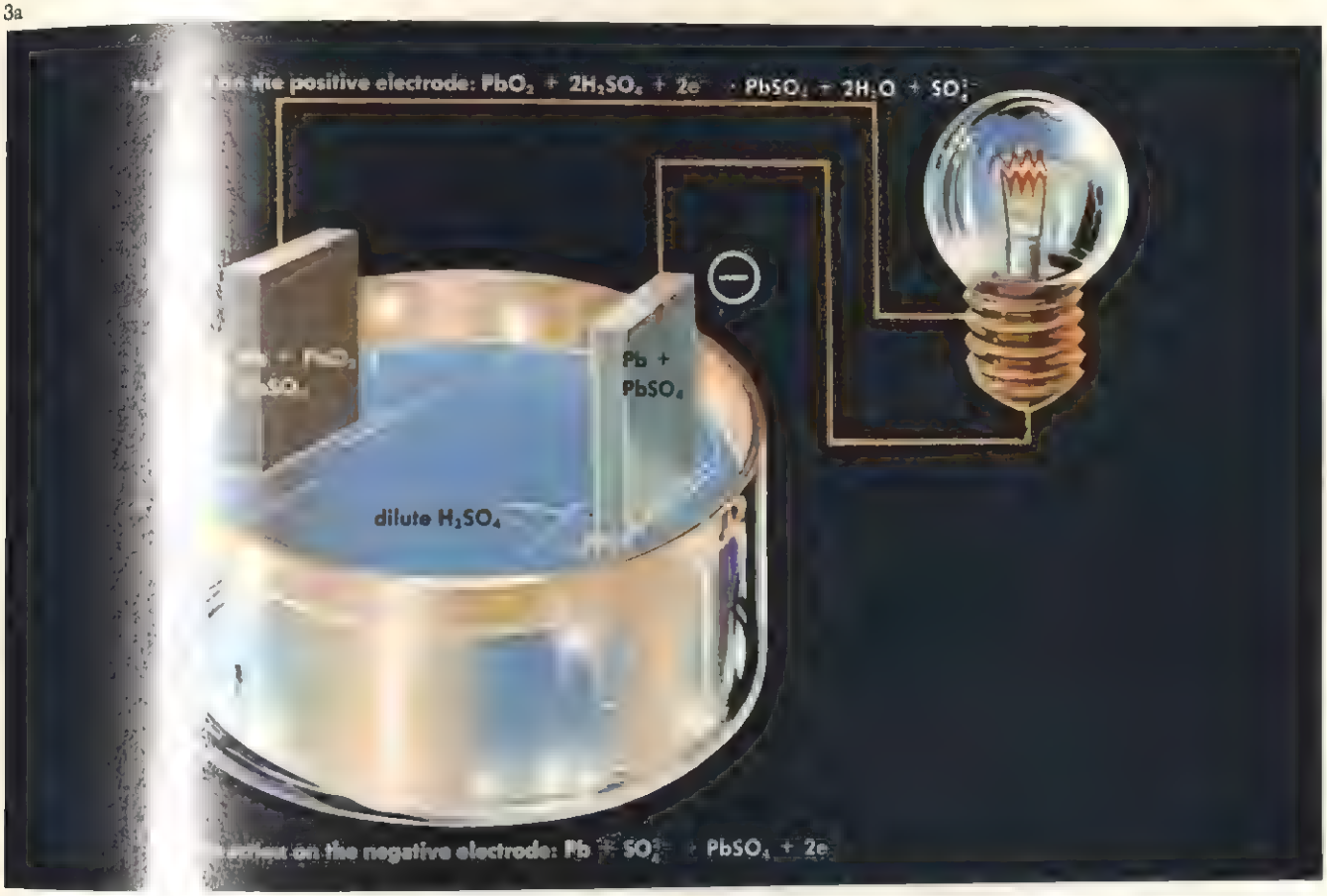
## NICKEL-IRON ALKALINE STORAGE BATTERIES

The only serious drawback to lead-acid storage batteries is their weight. They are thus unsuitable in applications where weight limits cannot be exceeded.

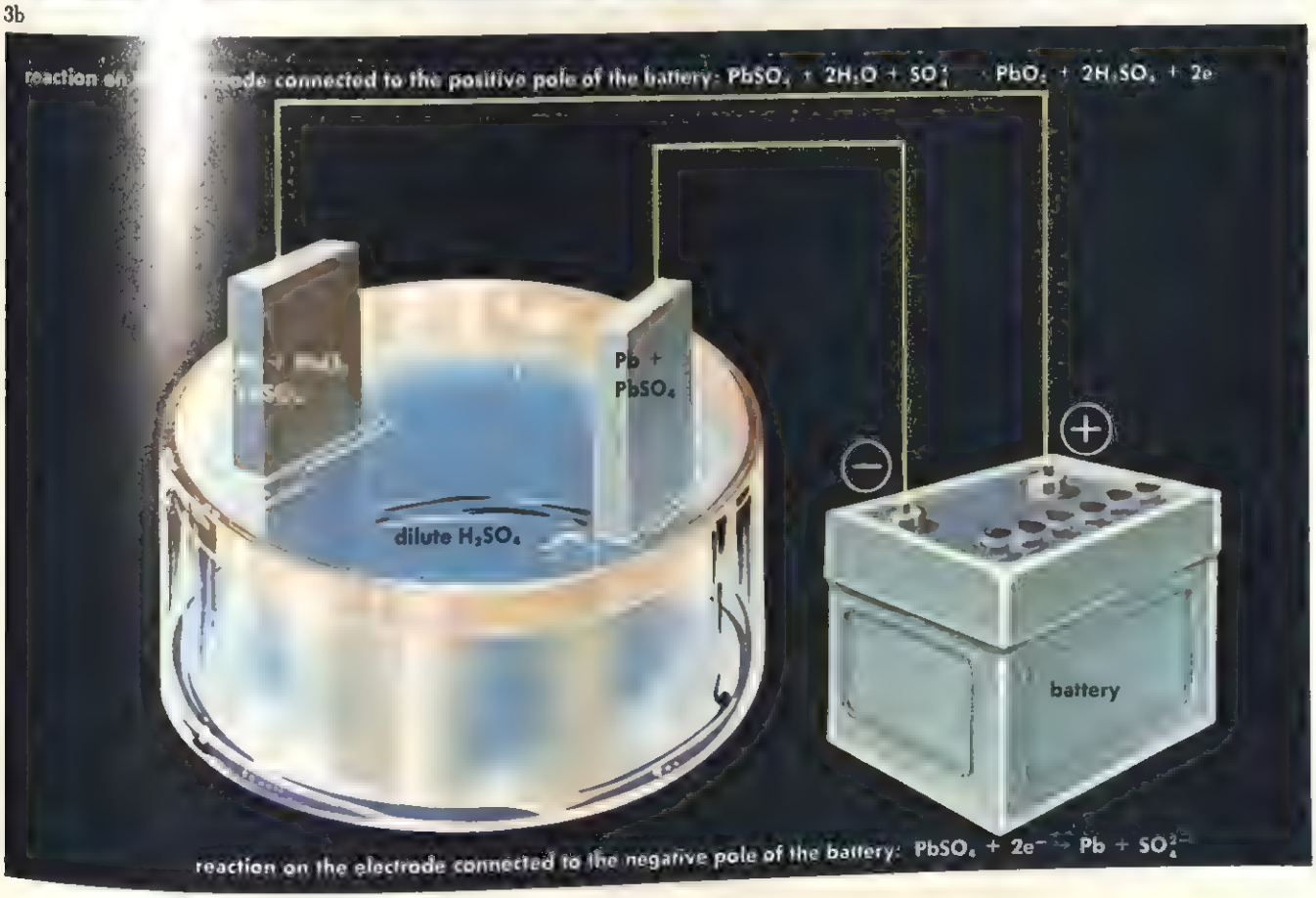
**DISCHARGE AND CHARGE REACTIONS OF A LEAD STORAGE BATTERY**—Illustration 3a shows the chemical behavior of a lead-acid battery during discharge. The negative electrode is made of spongy lead and lead(IV) oxide ($PbO_2$). Both electrodes are suspended in a diluted sulfuric acid solution. During discharge, the electrodes are progressively sulfated as the sulfuric acid is used up. Illustration 3b shows the charging process, which is the exact reverse of the discharging process. The electrodes return to their original composition and the supply of sulfuric acid is regenerated. The overall reaction is:

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O.$$

3a



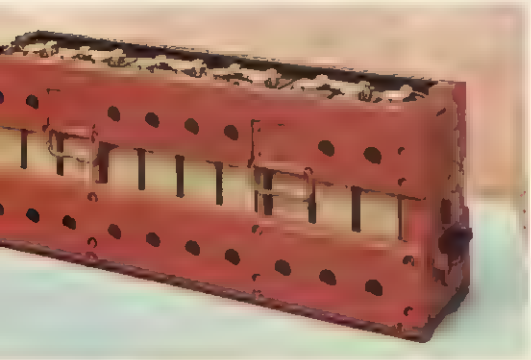

3b



4a

**ALKALINE ACCUMULATORS**—When weight is an important factor, lead accumulators are often replaced with lighter nickel-cadmium or nickel-iron storage batteries. The positive electrode of a nickel-iron storage battery consists of perforated nickel-steel cylindrical tubes filled with nickel(IV) oxide and splinters of metallic nickel. The negative electrode consists of iron mixed with iron(II) oxide. The two electrodes are suspended in a solution of potassium hydroxide containing a small amount of lithium hydroxide. This accounts for the name "alkaline" accumulator. In nickel-cadmium batteries, cadmium replaces the iron in the negative electrode. Illustration 4a shows a nickel-cadmium storage battery; illustration 4b is another nickel-cadmium battery whose chief use is to light railroad cars. Illustrations 4c and 4d show two nickel-iron batteries, the first with flat positive plates and the second with tubular plates.

4b

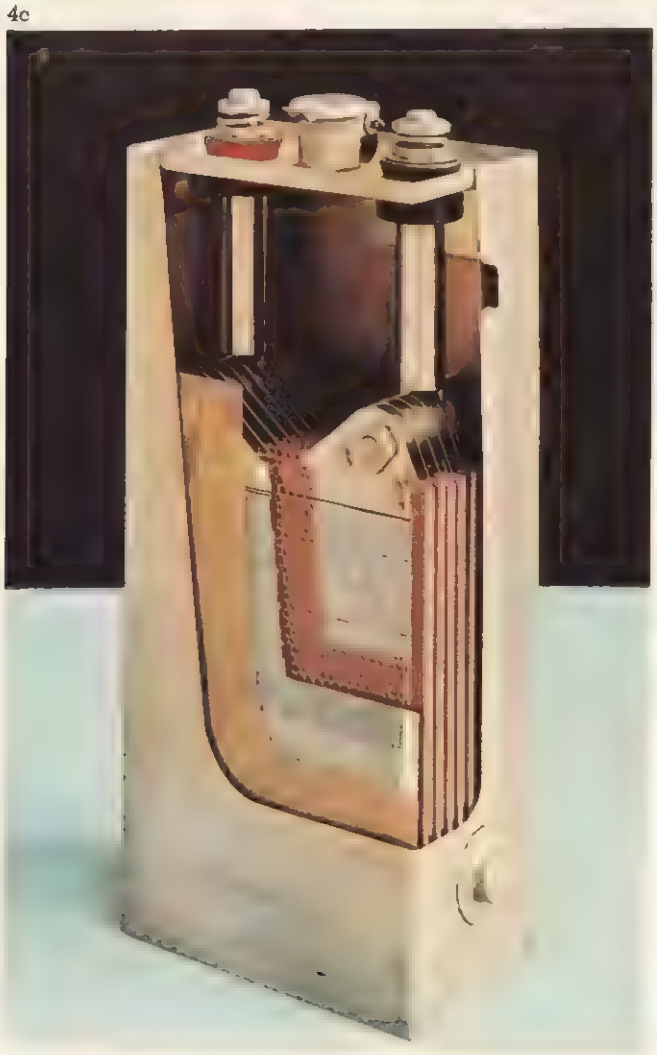


The nickel-iron alkaline storage battery, also known as the Edison battery, was especially developed for its lightness. This battery consists of a positive electrode made of a series of perforated nickel-steel cylindrical tubes filled with nickel(IV) oxide and splinters of metallic nickel, and a negative electrode made of iron mixed with iron(II) oxide. The two electrodes are suspended in a 21 percent solution of potassium hydroxide, KOH, containing small quantities of lithium hydroxide, LiOH. The Edison battery system is written out as follows (again in the direction of discharge):

$$\mathrm{Fe} \mid \mathrm{FeO} \mid \underset{(20\%)}{\mathrm{KOH}} \mid \mathrm{NiO_2} \mid \mathrm{Ni} \qquad (6)$$

The charge and discharge reactions of a nickel-iron alkaline battery cannot be given with a high degree of certainty because the oxides are hydrated in varying degrees and their precise compositions have not been established. In general,

4c



4d

**EDISON STORAGE BATTERY**—The illustration shows the chemical behavior of a nickel-iron alkaline storage battery during discharge. The reactions during charge and discharge are not known with great accuracy because the oxides undergo hydration in varying degrees and the compositions of the oxides are not precisely known. The yield of an alkaline battery is lower than that of a lead accumulator and its cost is higher. On the positive side, these batteries are much tougher and lighter than lead accumulators.

however, an i[illegible] the process is given by the reaction

$$NiO_2 + Fe + (KOH) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} NiOH_2 + Fe(OH)_2 + (KOH). \quad (7)$$

The potential [illegible]erence of an Edison battery is about 1.4 to 1.5 V. The battery is considered discharged if its voltage falls to about 1 V.

The yield of an alkaline storage battery is considerably below that of a lead accumulator, while its cost is usually higher. Despite these drawbacks, however, it offers certain advantages. These include toughness and lightness in comparison with lead-acid batteries.

Another type of storage battery similar to the Edison battery uses cadmium in the place of iron. Finally, the silver-zinc alkaline storage battery, with its high power and low weight, has met with considerable success.

## THE USES OF STORAGE BATTERIES

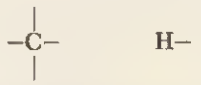
Lead-acid batteries, the most common type, are made in many shapes and sizes for a variety of uses classified as automotive, motive, or stationary. The automotive type is used in cars and trucks, to provide a short burst of power for starting the engine.

The second major class of storage batteries is used for motive power to operate electric trucks, golf carts, switch engines and mine locomotives, and also to provide power for the air conditioning and lighting systems of railway cars. These batteries are required to supply power for 3 to 10 hours instead of the few seconds needed to start a car or truck. They are designed to withstand frequent deep discharges instead of remaining almost fully charged. Also, weight and size, while limited in most cases, are not so critical as in the automotive battery. These considerations dictate a construction different from that of the automotive battery. The positive plates are thicker, and protected to prevent loss of active material that would otherwise occur in batteries alternately charged and discharged.

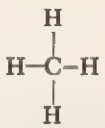
A third major class of storage battery, called stationary, is used to supply electrical power during emergencies, when the regular source fails. Such batteries are kept in hospital operating rooms, telephone exchanges, railway signal centers, and other places where a power lack might be disastrous. In the stationary battery, long life is much more important than weight or size. The plates are usually made heavier than in automotive or motive batteries, the acid volume is increased considerably while the specific gravity of the acid is reduced, and the insulation between plates is doubled or tripled.

# CHEMICAL BONDS | atoms in molecules

The valency of an atom, that is, its capacity to form chemical bonds, is often represented by long dashes. A bond is regarded as established when these dashes are linked with those of other atoms. For example, the tetravalent carbon atom and the monovalent hydrogen atom can be written as follows:



The methane molecule, consisting of carbon and hydrogen, is then written as follows:



This method of representing chemical bonds was introduced toward the beginning of the nineteenth century. Clearly, this was not done because chemists thought that atoms were spheres with small hooks on the outer surface, but rather because they were conscious of their ignorance of chemical bonding. The method was thus used for practical and instructional purposes.

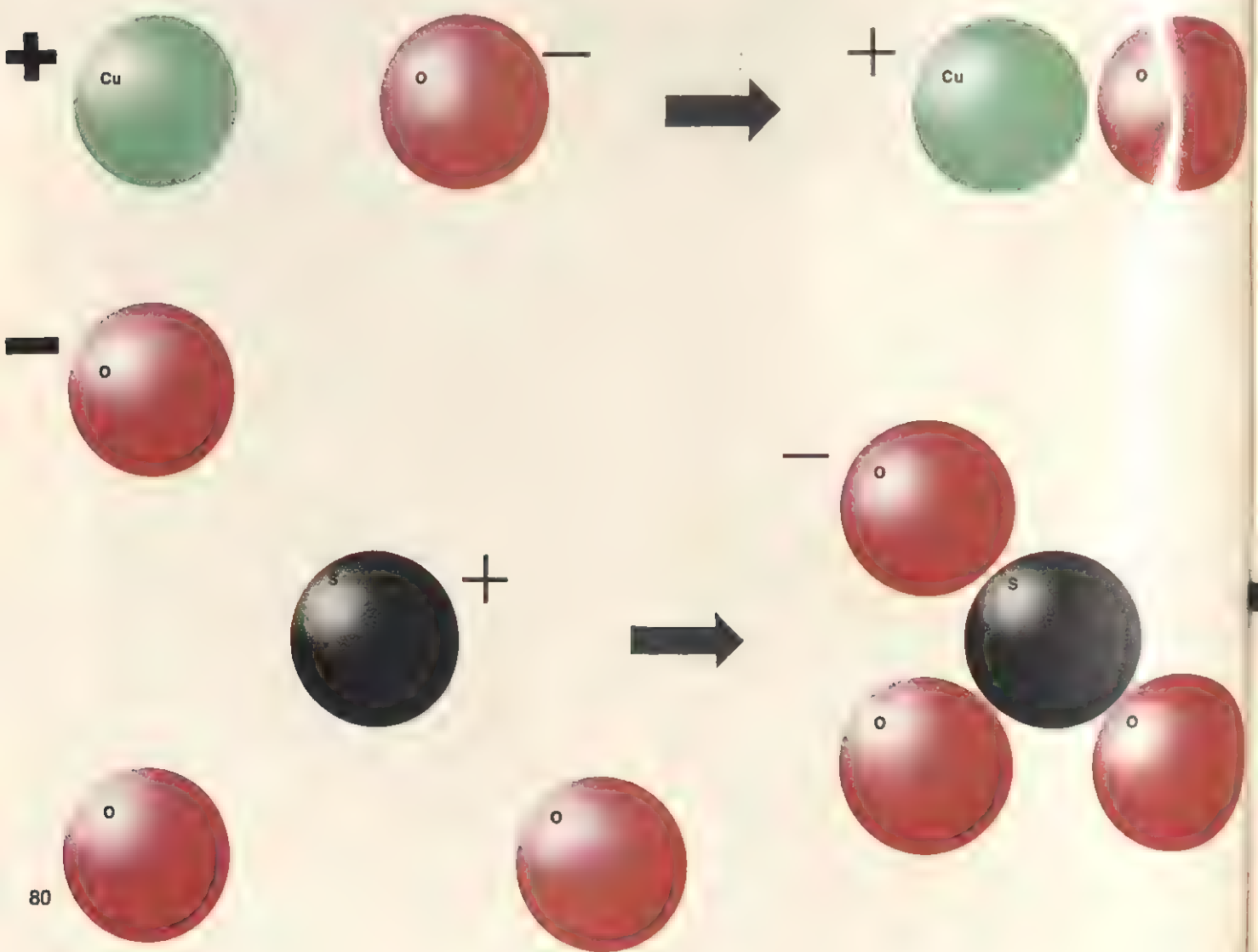
In practice, chemists had already arrived at the intuitive notion that chemical bonds might be electrical in nature, and that the explanation of bonding might be derived from the laws of electrical phenomena. Various substances dissociate into oppositely charged particles when they are in a fused state or in solution; these particles separate when a suitable electric field is applied. Positive particles (cations) and negative particles (anions) thus migrate to the electrode of the opposite sign. The mechanisms of these reactions are discussed in previous articles. Observations such as these led chemists to think that molecules might be held together by electrostatic attraction between the positive and negative particles. These views were developed primarily by the Swedish chemist J. J. Berzelius in his so-called dualistic, or electrostatic theory.

In actual practice, however, this theory would not explain certain very common phenomena. For example, it could not explain why diatomic molecules such as $H_2$ and $Cl_2$ are extremely stable. Moreover, there was no evidence whatever to view one of the hydrogen atoms of $H_2$ as a cation and the other as an anion.

## THE ATOM AS A SYSTEM OF ELECTRIC CHARGES

Today, scientists are in a position to say to what extent the theory of Berzelius is

1



acceptable and to what extent it is not. Modern methods of analysis, such as spectroscopy, x-ray diffraction, and quantum mechanics have greatly increased understanding of the structure of atoms and molecules. has thus been confirmed beyond doubt that chemical bonds are due to ...eraction between the electric fields ...ced by the charged particles (elec... of atoms.

The atom c... of a nucleus that contains two t... of particles, protons and neutrons. ... particles are known as nucleons. P... and neutrons have very similar m... roughly equal to the mass of a hyd... atom (about $10^{-24}$ grams). Proto... charged particles; they carry a ...ve charge of about $1.602 \times 10^{-19}$ ...lbs. Neutrons, however, as sugge... by their name, are electrically neu... If the mass of a proton or a neutro... assumed to be equal to one, a nucle... nsisting of Z protons and $N$ neutron... have a mass $A = Z + N$ (mass nu...) and a charge Z. However, each ...plete atom is electrically neutra... vause it contains a number of elec... revolving around the nucleus—a nu... equal to the number of protons with... e nucleus. Electrons carry a charge ...al in magnitude but opposite in sig... he charge on the proton. Electrons ... particles that move in a conductor ...ving an electric current. Because ... inertia is negligible, these particles ... ry mobile when they are not restrai... by electric fields. In fact, the mass o... electrons is so small that the mass of the atom may be considered as being concentrated within the nucleus. Although electrons are attracted by the nucleus, they do not fall into it as a result of their rapid motion in orbits.

The atoms of each element differ from the atoms of other elements in terms of the number of protons contained in the nucleus. This number is known as the atomic number. Thus, the nucleus of hydrogen (atomic number = 1) contains one proton. The nucleus of neon (atomic number = 10) contains 10 protons, and so forth.

## THE IONIC BOND

The outermost electrons of an atom are those most weakly attracted to the nucleus. These electrons—called valence electrons because of their effect on valence—are, therefore, the most easily removed from the atom. When this is done, the atom becomes a cation (positive ion) because it has an excess of positive charge. The energy needed to remove an electron —the ionization energy—differs from one atom to another. In general, the atoms of metallic elements have rather low ionization energies. They therefore form cations with comparative ease. Sodium (Na), for example, readily loses an electron and becomes a sodium ion ($Na^+$).

Other atoms, however, become more stable when an electron is added to the outermost shell. (These atoms are usually nonmetallic.) This additional electron converts these atoms into anions.

2

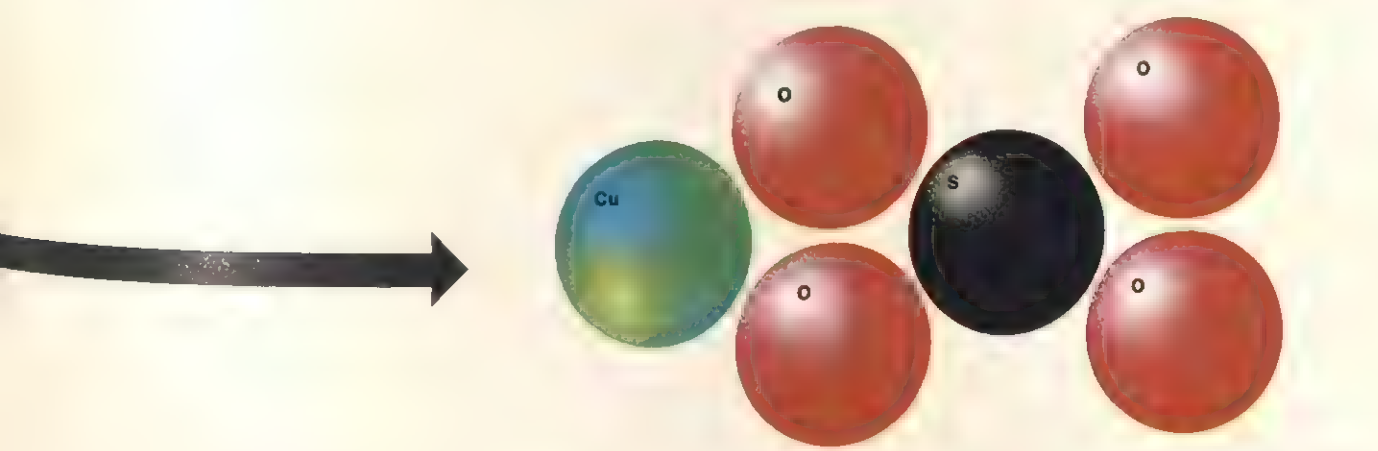
| | RELATIVE MASS | CHARGE (1 unit = $4.8 \times 10^{-10}$ electrostatic units or coulombs) |
|---|---|---|
| proton | 1 | 1 |
| neutron | 1 | +0 |
| electron | 1:1,840 | −1 |

**MASS AND CHARGE IN THE NUCLEUS**—This table illustrates the masses of the elementary particles of the atom, with the mass of the proton or the neutron taken as one. The second column in the table shows the electrical charge of each particle.

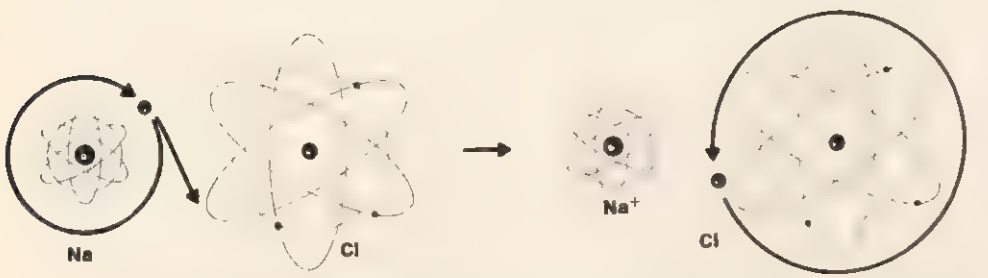
Chlorine (Cl), for example, readily accepts an electron and becomes a chloride ion ($Cl^-$). The atoms of these elements are said to have a high electron affinity. This approach permits a refinement of the electrostatic theory. When two atoms such as sodium and chlorine collide, the sodium atom loses an electron, which is immediately picked up by the chlorine atom. This produces a sodium ion and a chloride ion, which are then attracted to each and held together by electrostatic force. The two ions together are called an ion-pair; the bond is known as an ionic or electrostatic bond.

## THE COVALENT BOND

Today's chemists use a model of atomic structure that lends itself to a far more general explanation of chemical bonds than the old electrostatic theory. This model, however, requires that the charged particles of a bond no longer be thought of as statically opposed to each




**BERZELIUS' DUALISTIC THEORY**—These diagrams illustrate the dualistic theory put forward by the Swedish chemist J. J. Berzelius. Copper (Cu), positive, combines with oxygen (O), negative, to form copper oxide, CuO. Sulfur (S) combines with oxygen to form sulfur trioxide, $SO_3$. Since copper is more positive than oxygen is negative, a residue of positive charge remains on the copper oxide. Sulfur trioxide, on the other hand, maintains a residue of negative charge because of the greater negativity of oxygen. These two molecules thus have residual charges of opposite signs and can, therefore, combine to form a molecule of $CuOSO_3 = CuSO_4$, copper sulfate.




**GASEOUS SODIUM CHLORIDE**—This illustration shows how a molecule of gaseous sodium chloride is formed. The sodium atom (Na) loses an electron and becomes an $Na^+$ ion. This electron is transferred to the outer orbit of the chlorine atom, which thus becomes a $Cl^-$ ion. The result is an electrostatic or ionic bond between the two ions. As a result of the transfer of the electron from the sodium atom to the chlorine atom, the former decreases in size and the latter increases in size.

other. The particles that collide with each other during the course of a chemical reaction are part of a world swarming with electric charges—electrons, polar molecules, ions, and so forth. The farther electrons are from the influence of the nucleus, the more freely they are able to move. Charges in motion constitute electrodynamic forces, simply because they are moving (a macroscopic example is two wires carrying electric currents that attract or repel each other depending on the relative directions of the two currents). Thus, given a system of charges in motion, a kind of dynamic equilibrium will occur. In more rigorous language, the energy of the system of charges tends to assume a minimum value.

Consider an isolated atom A that has attained equilibrium; the electrons of this atom revolve about the nucleus in orbits that satisfy the conditions of minimum energy. If a second atom B, also in a state of equilibrium, collides with atom A, the equilibria at the moment of impact are destroyed. The electrons and protons of atom A suddenly come within the radius of action of the electrons and protons of atom B, and vice versa. The system is thus under pressure to attain a new state of equilibrium. In this new equilibrium some of the outer electrons of both atoms no longer revolve in orbits that belong to one of the nuclei. Rather, they become established in orbits that surround both the nuclei. The net effect is that the two atoms have united in order to share some of their outer electrons. In the case of hydrogen, two identical atoms, each consisting of a proton and an electron, unite to form a molecule ($H_2$) in which the electrons (two in all) revolve in a molecular orbit around both nuclei.

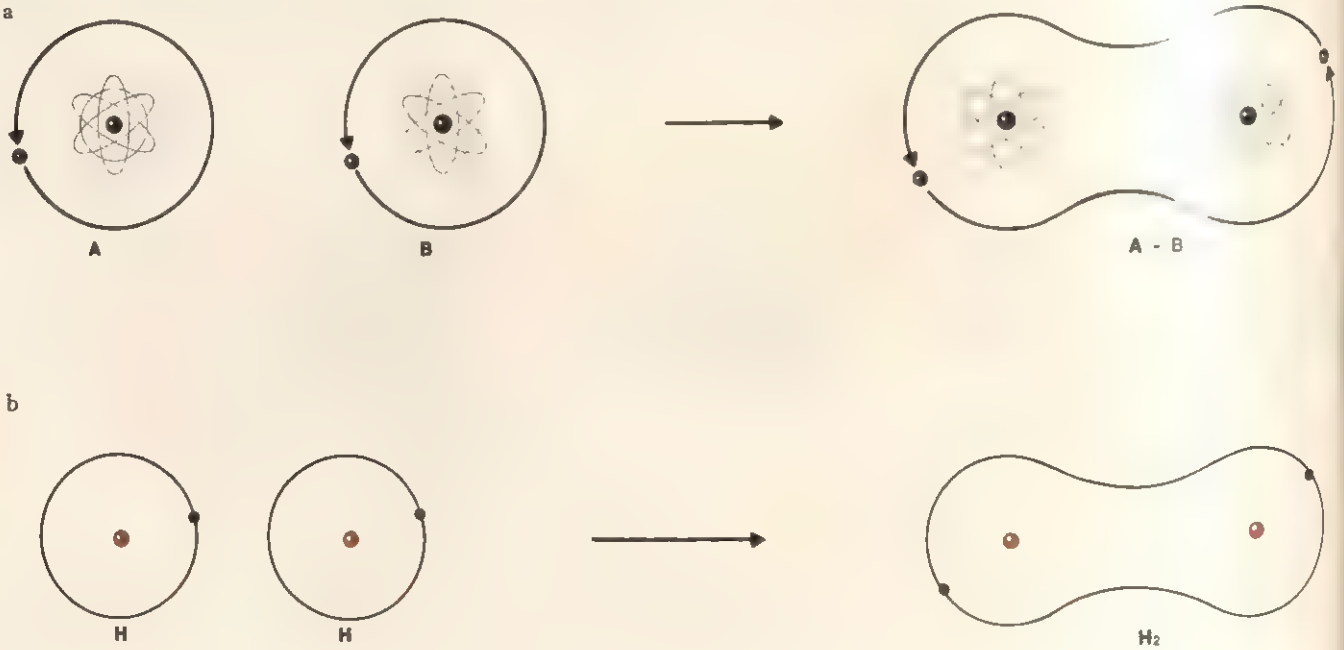
To say that a bond is formed because the atoms share their outer electrons does not really constitute an explanation. Rather, it is at best a description. From this point of view the electrostatic bond seems more comprehensible despite the fact that it does not explain the bonds in molecules such as $H_2$ and $Cl_2$. On the other hand, the shared-electron model does not explain a great deal more. In reality, emphasis must be placed on the interactions between the particles in the system of moving charges. These interactions that are not purely electrostatic, but rather electrodynamic. These interactions are determined by mathematical calculations. When translated into descriptive form, the results of these calculations appear as the shared-electron-pair bond. This type of bond is called a covalent bond.

## BOND POLARITY

Has the theory of the electrostatic bond been made obsolete by the theory of the



**COVALENT BONDS**—When an atom B collides with an atom A, a number of the outer electrons orbit around both nuclei. In other words, the two atoms now share some electrons (illustration 4a), forming a particle that is more stable than the individual atoms. The formation of a hydrogen molecule from two separate hydrogen atoms (illustration 4b) is an example of the covalent bond



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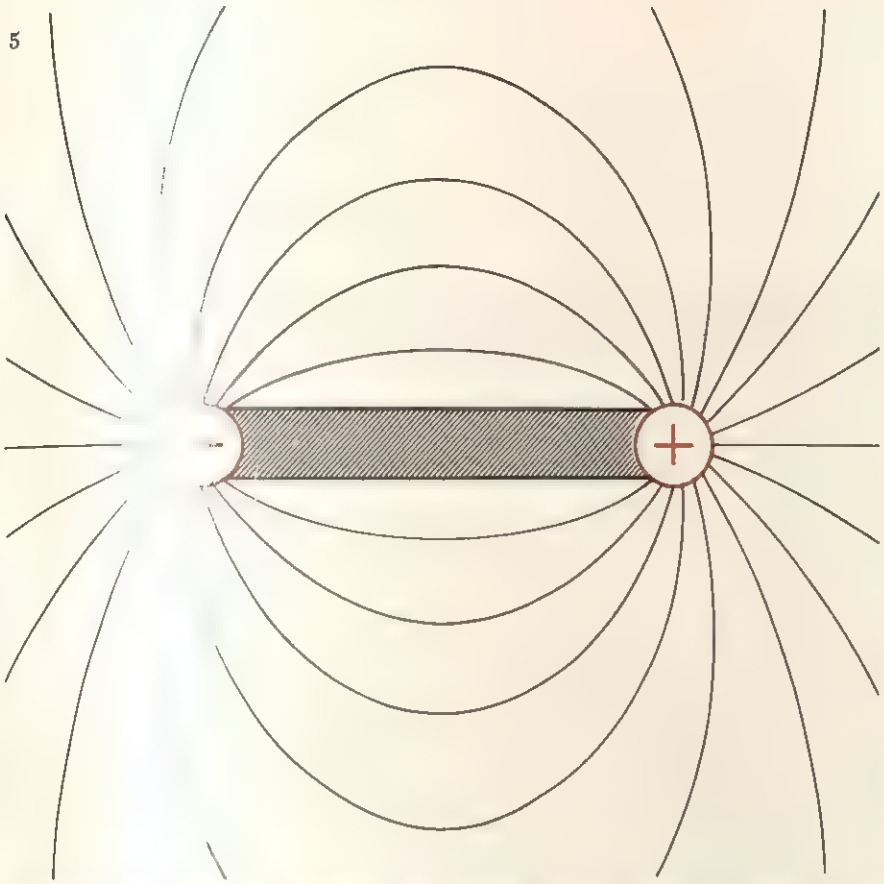
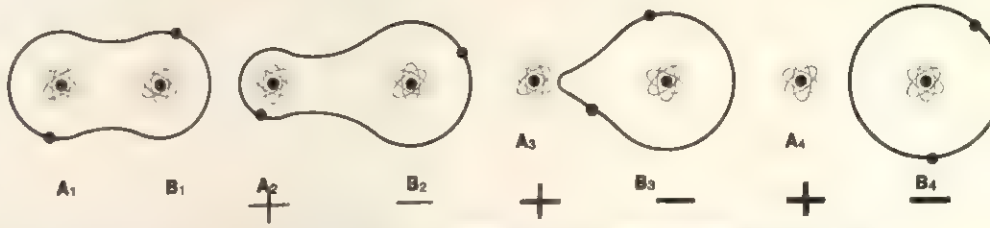


**A DIPOLE** — The illustration represents the electrostatic field set up by a dipole; that is, a molecule in which the center of positive charge does not coincide with the center of negative charge. Although a molecule of this type is, as a whole, neutral, it will always be surrounded by an electric field.

covalent bond are different bond types possible. To answer this question, consider a neutral hydrogen atom, H, a hydrogen molecule, $H_2$, and a molecule of hydrogen chloride, HCl. For each of these particles, there is no net electric charge because the total number of protons is exactly balanced by the total number of electrons. The distribution of charges within a particle, on the other hand, may differ. The centers of positive and negative charge coincide in H and $H_2$, but not in the case of HCl. In fact, in HCl the center of positive charge is displaced toward the hydrogen atom and the center of negative charge is displaced toward the chlorine atom. A molecule of HCl, whose overall charge is zero, therefore acts like an electric dipole and sets up an electric field around itself. This happens because the H and Cl nuclei are not identical. The Cl nucleus contains more protons and thus exerts a greater attractive force on electrons. Put another way, chlorine is more electronegative than hydrogen. Therefore, when an H atom and a Cl atom react and a covalent bond is established, the electrons spend more time orbiting around the chlorine atom. The electron cloud around the chlorine atom is thus much denser than the negative charge cloud surrounding the hydrogen atom. When a covalent bond is formed between two identical atoms, on the other hand, the resulting molecule is symmetrical with respect to charge; that is, no polarity exists. If the atoms are different, the molecule is always polar, although the extent of the polarity may differ from case to case.

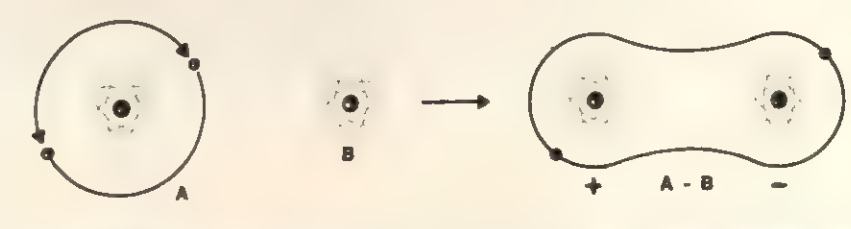
In the extreme, if the electronegativity of the two atoms A and B differs by a very large amount the result is that the bonding electrons will spend all of their time around the more electronegative atom. In other words, formation of the bond constitutes an exchange of electrons. The outermost electron(s) of one atom passes to the other atom, thus forming a pair of oppositely charged ions. The ionic bond may thus be viewed as the limiting case of a highly polar covalent bond. Displacement of bonding electrons occurs also when the molecular orbit extends around both atoms almost equally, but the electron pair comes from only one of the two atoms. This type of bond is called a dative or coordinate covalent bond. Clearly, the donor atom is the one that assumes the positive polarity.

6




**FROM COVALENT BOND TO IONIC BOND**— This illustration shows the gradual transition from the covalent bond that unites atoms $A_1$ and $B_1$ to the ionic bond that unites atoms $A_4$ and $B_4$. This transition occurs as the difference in the electronegativity of the two atoms increases. In the extreme, the outer electron of one atom is transferred to the other atom, forming a pair of oppositely charged ions.

7




**THE COORDINATE COVALENT BOND** — The coordinate covalent bond is the result of yet another type of electron displacement. Here the electrons in the molecular orbit revolve around both nuclei, but these electrons came from just one of the two atoms. The donor atom, atom A in this case, thus assumes a positive polarity.

# ATOMS AND CRYSTALS | the properties of crystals depend on atomic order

Steel, heated until it glows and then cooled rapidly, is harder than if it had been cooled slowly. During such rapid cooling iron and carbon atoms reposition themselves in a way that gives the steel its hardness.

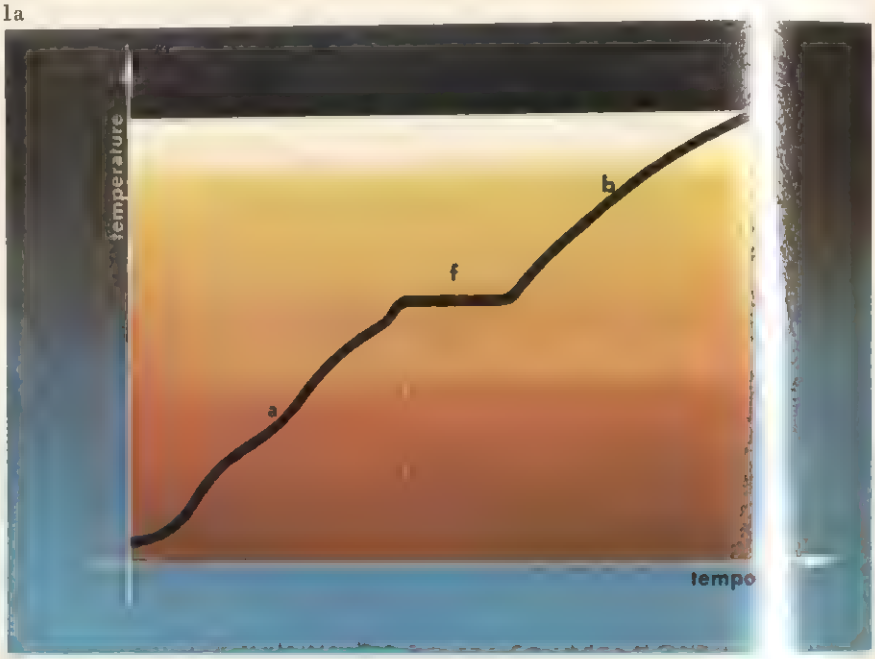
In the 19th century the thrust in chemistry was toward the formulation of a theory of matter to explain the laws of chemical reaction and to define precisely the concept of the molecule; the result was the modern atomic theory of matter. Subsequently chemists and physicists began studying the arrangement of atoms in molecules and of molecules in solid bodies. Today, as a result of these theoretical studies, it is possible to synthesize new compounds that are very hard with a high melting point, as well as those that are very soft with a low melting point. Quite generally substances can be "tailor-made" for many specific purposes.

Today's knowledge of matter extends far beyond elementary properties such as hardness and refractoriness. It is now possible to explain the reason for certain properties of matter; for example, it has been established that the color of different solid bodies is controlled by the irregular arrangement of the atoms inside them. The properties and characteristics of matter in the solid state fall generally into two areas: those that are caused by regular and symmetric atomic arrangements, and those that are caused by irregularities and a lack of symmetry. The distinction between the two is not clear-cut, but the two classifications allow certain generalizations to be made.

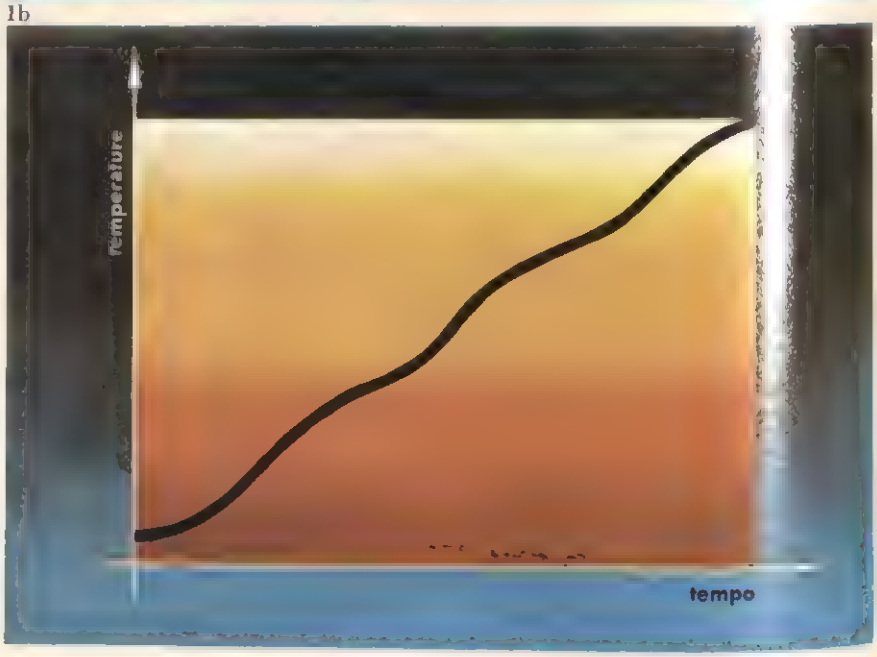
The most obvious properties of solid matter are based on the regular arrangement of atoms, but many other, less apparent, properties depend on isolated irregularities found even in the most regular of crystals. Such imperfections explain the rapid solidification of solids from a solution as well as from their own

**THE CHARACTERISTICS OF SOLIDS**—Any substance that has a crystalline structure in the solid state has a well-defined melting point. When the substance is heated, it re-

1a

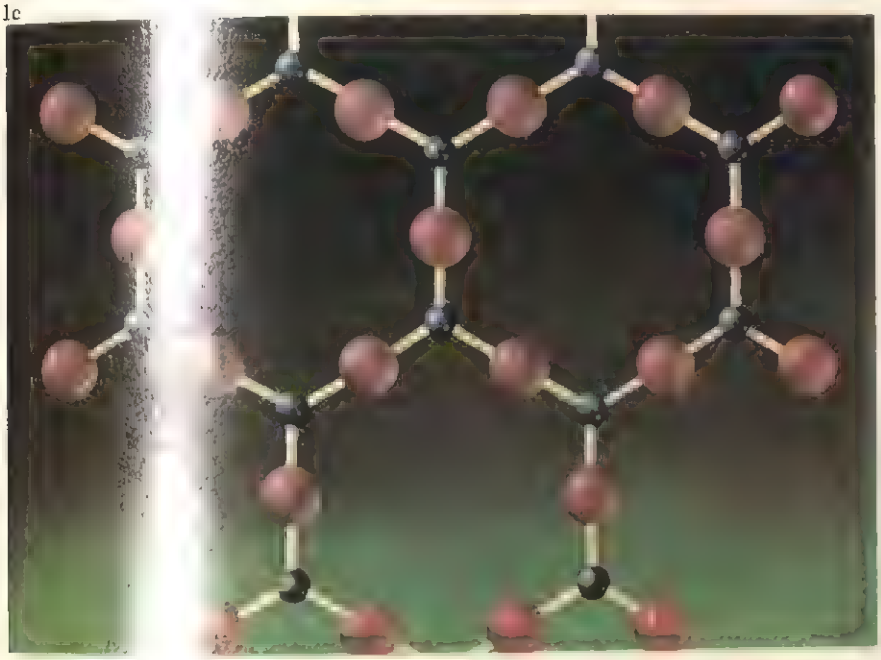



1b



mains solid up t
perature it beco
oint; above that tem-
uid. A substance is
heated by supplying energy—more precisely, heat—to it. Illustration 1a shows what happens during this process: the substance stores this energy in its mass, raising its temperature (section **a** of the curve). A dramatic change takes place once the melting temperature is reached. The heat first accelerates the oscillating motion of the atoms of the solid. In solids, as opposed to liquids and gases, the atoms are fixed in one position around which they vibrate more or less rapidly depending on the temperature. Once the melting point is reached, the atoms vibrate so rapidly that they overcome the forces of attraction that held them together in the form of the crystal lattice, and the atoms break away from each other. Until all the atoms have broken away from each other and a liquid is formed, the energy supplied no longer increases the temperature of the substance but only liquefies the substance by destroying its crystalline structure. As a consequence, the temperature of the substance remains unchanged during the time melting takes place (section **f** of the curve). If heating continues, the temperature will rise once again (section **b** of the curve). This heat curve, with its typical leveling off at the melting temperature, is characteristic of solids. No two solids of different composition have the same melting point, which is why the melting point can be used in analysis to identify solids. Impurities in a substance, however, can cause the melting temperature to vary considerably.

1c



1d

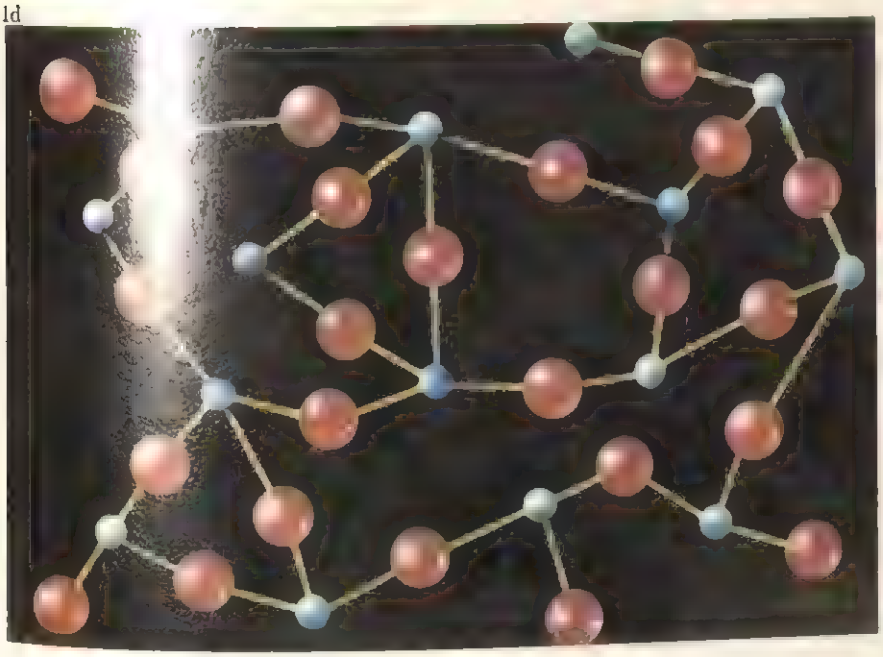


Illustration 1b shows the heat curve of a liquid or a substance that appears to be solid but has the properties of a liquid—glass, for example. This type of melting curve shows no leveling off.

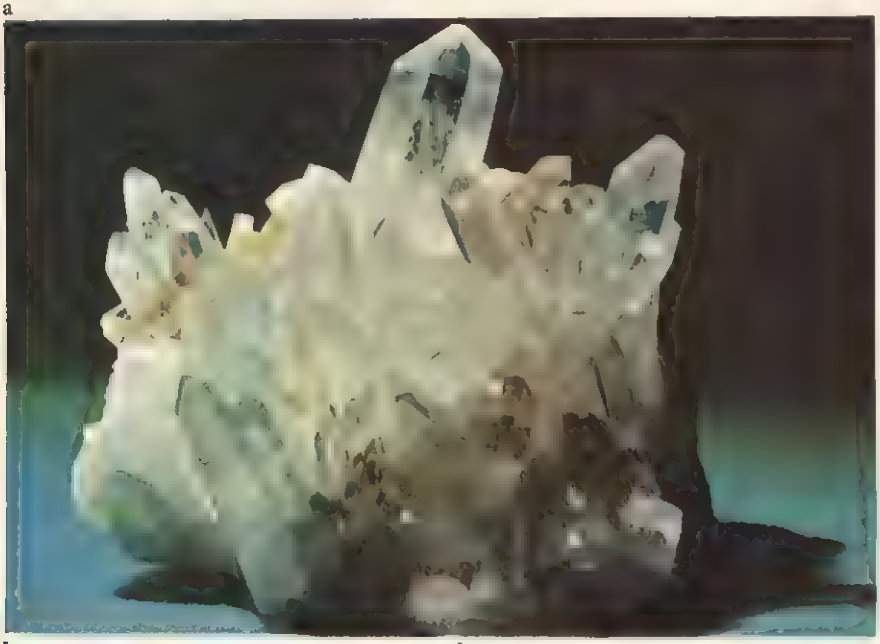
It is possible to interpret the various characteristics of the heat curves of a solid or liquid by examining the arrangement of the atoms inside the substance. Illustration 1c shows how the atoms in a solid are arranged in simple, regular formations that are periodically repeated. When the atoms are heated they vibrate around the positions shown. At a certain level of vibration the atoms break away from these positions and, in so doing, melt the solid.

In a liquid or other substance with a noncrystalline structure, the positions occupied by neighboring atoms are irregular, as shown in illustration 1d. As the temperature, and therefore the agitation of the molecules, increases, the amounts of energy in the molecules increase. The less stable structures break down first; as the agitation increases, the more stable ones break down. Because noncrystalline solids generally do not have definite transition points, they soften, in the ordinary sense of the word, at a gradual rate with increasing temperature.

molten liquid, why metals are ductile, why metals acquire hardness under heat treatment, and why alloys are harder than their constituent elements. Slight imperfections are also responsible for semiconductors having special current-carrying properties, or for the fact that ionizing radiation can radically change the properties of a substance. Imperfections account for the fact that a metal subjected to certain stresses becomes more susceptible to corrosion than one not so subjected, and for the fact that a perfectly pure and transparent crystal may exhibit color without any sort of impurity being introduced into it—the list of such properties is almost endless. A study of the chief characteristics shown by solids is essential to deducing the arrangement of the atoms inside them.

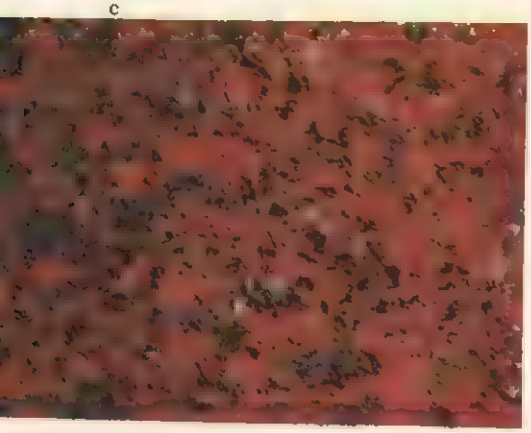
2

a

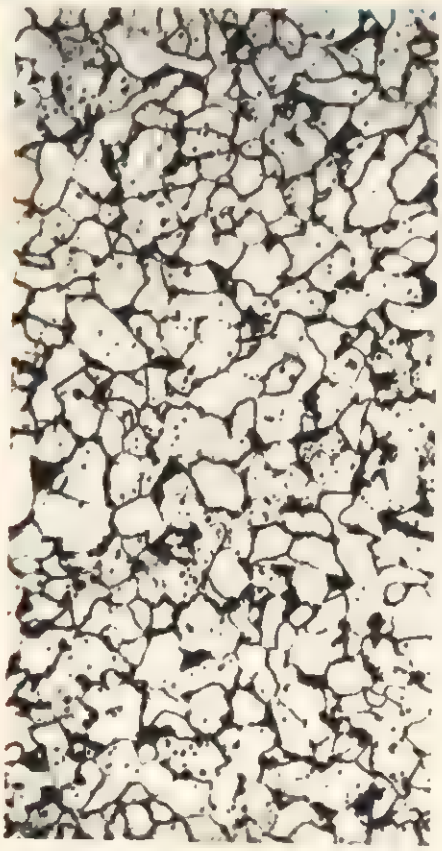


b

c



d



**SOLIDS IN THEIR CRYSTALLINE STATE**—Only substances with a fixed melting point can be properly called solids. But there are also other basic characteristics of solids. All solids have a crystalline form. When producing a solid, by solidifying it from liquid, by evaporating a solution, or by condensing a vapor, it is possible to cause the solid to grow, or accrete, in some regular geometric form. Illustration 2a shows a quartz crystal, silicon dioxide ($SiO_2$), that is regular in shape.

Solids are formed of either a monocrystal—one single crystal—or of many adjacent monocrystals fused or in contact with each other. An isolated crystal, or a projecting crystal such as the one in illustration 2a, is said to have the crystalline habit typical of the substance. Illustration 2b, on the other hand, shows an association of pyrite crystals projecting from a mass of pyrite. The projecting crystals are characteristically cubical. The mass from which they project, also formed of pyrite (iron disulfide), contains similar monocrystals which, because each of them grew in the space left free by its neighbor, are in contact with each other. The exterior appearance of the monocrystals does not show the characteristic habit. Even in the compact mass the crystals are well formed and have properties similar to those of the projecting crystals. If the compact mass were hammered to pieces, the fragments would appear similar in shape to the projecting crystals.

If a solid substance consists of a mass of large and small (sometimes microscopic) monocrystals, the mass is called a polycrystalline mass. The sample of granite shown in illustration 2c is a simple polycrystalline mass. The main constituents of the granite are monocrystals of quartz, feldspar, and mica.

Special techniques are used to reveal crystalline structure that is invisible to the unaided eye. Illustration 2d, for example, is a photograph made through a microscope that shows the complex polycrystalline structure of a metal. Isolating one of the grains from which this mass is formed would reveal a monocrystal; however, the monocrystal would not display its characteristic habit because its shape has been modified by the presence of neighboring crystals.

The properties of monocrystals are important because from them properties of polycrystalline substances may be deduced. The study of solid-state physics has greatly stimulated techniques of producing monocrystals. When scientists first began to study the basic properties of solids, they used mineral crystals (usually polycrystalline) because samples were readily available that showed the characteristic habit. Later a need arose for isolated crystals produced from substances other than those found in nature, such as metals, alloys, and the crystals of many synthetic, inorganic substances.

# STOICHIOMETRY | calculating chemical composition

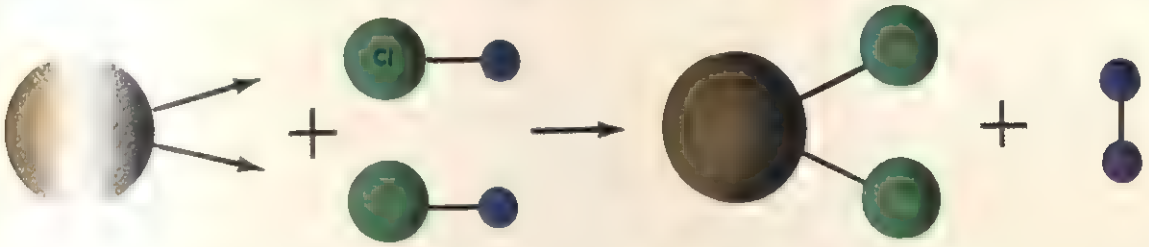
When a chemi ed with a chemical formula (HNO ample, the formula for nitric acid) nows what it represents. The form ls him that a molecule of nitric a ntains one atom of hydrogen, one ogen, and three of oxygen. It do tell him, however, how these ato arranged—in other words, it tell nothing about the structure of t lecule. This type of formula is, th called an empirical formula, to show that it conveys only a limited amount of information about the molecule.

The subject of this article is the interpretation of such information—in particular, how the weight of the molecule is a function of the weight of its atoms. Since each atom has a specific atomic weight, the formula reveals the relative weights of the different elements in the compound.

even though the number of hydrogen atoms in the molecule is double the number of oxygen atoms.

The nitric acid molecule is another interesting example. The formula is $HNO_3$, and the calculation of molecular weight is as follows:

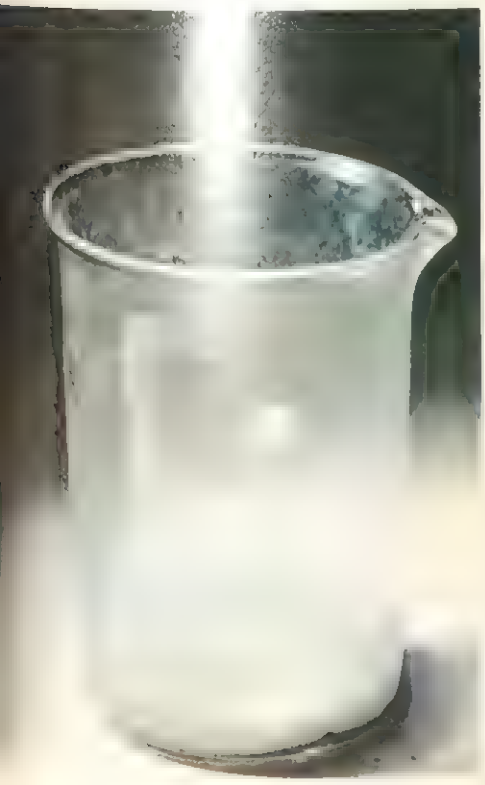
| | |
|---|---|
| one atom of hydrogen: | 1.008 |
| one atom of nitrogen: | 14.008 |
| three atoms of oxygen: | 48.000 |
| | 63.016 |




1a

**FORMATION O** hydrochloric a taining a few g chloride and h follows: Zn + **CHLORIDE**—If a little ided to a beaker con- zinc, the result is zinc gas. The reaction is as $H_2\uparrow$ + $ZnCl_2$.

1b



## MOLECULAR WEIGHT AND ATOMIC WEIGHT

Molecular weight is the sum of the atomic weights of the atoms that form a molecule. As an example, the formula for water is $H_2O$; thus, the molecule contains two atoms of hydrogen and one atom of oxygen. The molecular weight of $H_2O$ is the sum of the atomic weights of the two hydrogen atoms and the one oxygen atom:

$$\begin{aligned} 2H: 2 \times\ 1.008 &= \ 2.016 \\ O: 1 \times 16.000 &= 16.000 \\ &\overline{\qquad\quad 18.016} \end{aligned}$$

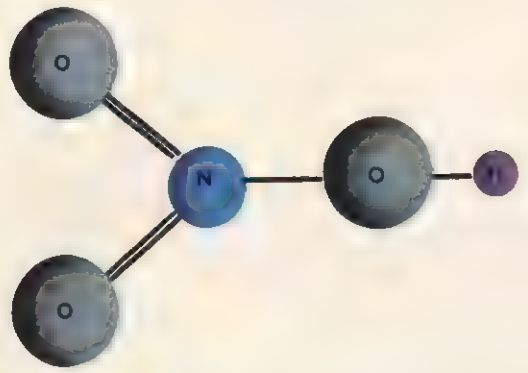
18.016 is thus the weight of a molecule of water expressed in atomic weight units. While the actual weight in grams of a molecule of water is not known (although it may be calculated by converting atomic weight units into grams), the ratio between the weight of the hydrogen and the weight of the oxygen in $H_2O$ is known. Given that the hydrogen atoms in a molecule of water weigh 2.016 and the oxygen atom 16.000, simply dividing the weight of the oxygen by the weight of the hydrogen gives the ratio desired: 7.94. Water thus contains almost eight times as much oxygen as hydrogen by weight.

The molecular weight of nitric acid is thus 63.016. The oxygen fraction by weight is 48.000/63.016 or 0.762. In other words, oxygen accounts for more than three quarters of the weight of nitric acid.

## APPLYING STOICHIOMETRIC CALCULATIONS

The formula of a molecule permits calculation of the ratios, by weight, of the atoms it contains. The converse problem can also be solved. Research into the composition of chlorophyll b, for example, shows that its molecular weight ranges from about 905 to 910. Analysis shows also that the chlorophyll molecule contains the metal magnesium, and that its proportion in the molecule is roughly 3 percent by weight. The question is: how many atoms of magnesium does one molecule of chlorophyll contain? Since the atomic weight of magnesium is 24.32, the ratio of this figure and the total molecular weight is 24.32/907 (taking 907 as the approximate molecular weight), or 0.027; in other words, nearly 3 percent by weight. The conclusion from this calculation is that the chlorophyll molecule contains exactly one atom of magnesium. If

2




**NITRIC ACID**—The empirical formula $HNO_3$ indicates only the number and types of atoms in the acid molecule. The structural formula, shown in the illustration, shows how the atoms are combined and the nature of the bonding.

it contained two, the ratio would have been $48.64/907 = 0.0537$. In actuality, the ratio was nowhere near this figure). Using the same general method to work out the proportions of the other atoms in the molecule, the empirical formula $C_{55}H_{70}MgN_4O_6$ has been derived for chlorophyll b.

Stoichiometry can thus be used to work out the formulas of chemical compounds. It can also be used to calculate the correct quantities of reagents for the preparation of compounds. Suppose, for example, that zinc chloride ($ZnCl_2$) is to be prepared, using hydrochloric acid (HCl) and zinc (Zn) as the reagents. How much zinc, and how much hydrochloric acid is required, for example, to produce 100 g of zinc chloride? The reaction is:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2.$$

The first step is to look at the atomic and molecular weights of these substances.

$$Zn = 65.37$$
$$HCl = 36.46$$
$$ZnCl_2 = 100.82$$

The amount of zinc needed is calculated as follows: If 65.37 parts of Zn are needed to form 100.82 parts of $ZnCl_2$, then let $x$ be the number of grams of zinc needed to get 100 g of $ZnCl_2$. The resulting ratio is:

$$ZnCl_2 : Zn = 100 : x.$$

Numerically, this is

$$100.82 : 65.37 = 100 : x.$$

Hence

$$x = \frac{(65.37)\ (100)}{100.82} = 64.9 \text{ g zinc.}$$

Similarly for hydrochloric acid, the quantity needed is

$$100.82 : (2 \times 36.46) = 100 : x$$

$$x = \frac{(100)\ (2 \times 36.46)}{100.82} = 72.3 \text{ g HCl.}$$

However, while hydrochloric acid is a solution, the HCl that enters this reaction is a gas. The most practical way to handle HCl is to dissolve it in water. To determine how much of the acid solution is required, however, it is necessary to determine the concentration of the solution; this reveals the weight of solution needed.

This type of stoichiometric calculation is used to work out the quantities of substances required for industrial chemical reactions, although certain adjustments may have to be made in the calculations described above. In the case of mass-produced, low-cost zinc chloride, for example, the zinc introduced into the reaction chambers is not of the purest quality. Since impurities contribute to the weight but not to the production of zinc chloride, however, the quantity of zinc has to be increased slightly for every hundred grams of $ZnCl_2$ produced.

## TITRATION

One important use of stoichiometry is in titration. This can best be explained by an example. Consider an aqueous solution of caustic soda, and suppose that the quantity of NaOH dissolved in the solution is desired. Direct analysis, although possible, would be a long and costly process. Titration is a much simpler method. In titration an acid is added to the solution until it is neutral. Since caustic soda—a strong base—that is to be titrated, the acid added will have to be a strong acid. Hydrochloric acid will be used since it can be introduced drop by drop into the NaOH solution up to, but not beyond, the

3

**CHLOROPHYLL**—The molecular weight and composition of chlorophyll were worked out by stoichiometry, which shows, among other

point of neutrali… he reaction is: HCl +NaOH → NaCl …O. The base solution (which tu… …mus paper blue) is gradually neutr… …by the addition of the acid. The s… …aCl) is the product of the reaction … point of neutrality the color of th… … paper remains unaltered. The p… …e of base in the solution, that is … …r of the base, is given by the a… …f acid added.

Titration ca… …ried out on a sample of solutio… … extremely simple. The point at … …he solution reaches neutrality is shown by an indicator—a substance that changes color when the solution in which it is immersed turns from acid to base or base to acid.

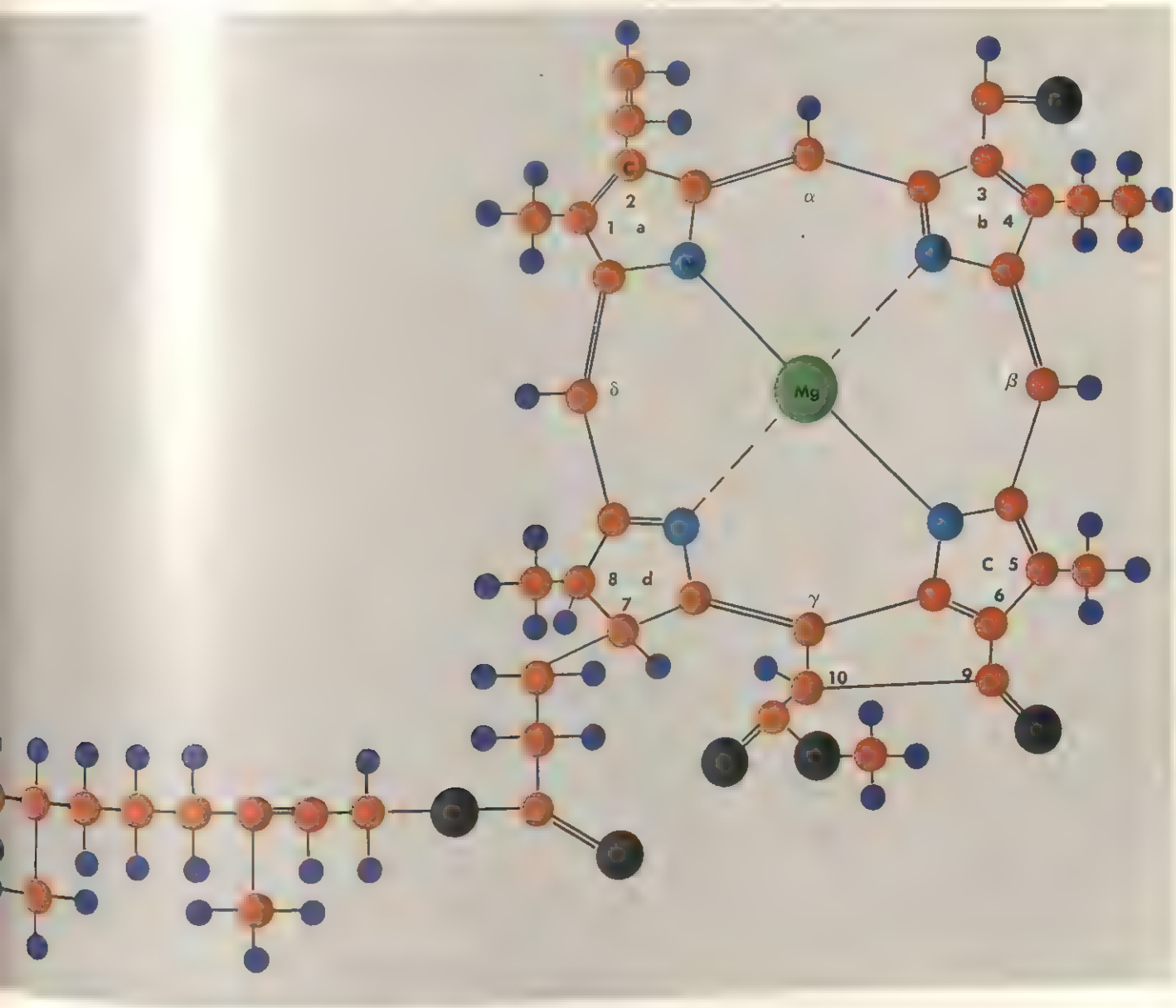
Electrometric titrations are those in which the point of neutrality, or end point, is detected by electrical measurements. Four types of electrometric titrations are utilized: potentiometric, conductometric, amperometric, and coulometric.

The usual potentiometric titration arrangement is to have two electrodes, one an indicator electrode in the solution containing the sample being titrated, the other a reference electrode, external to the sample vessel and connected to it by means of a salt bridge. The indicator electrode is chosen to respond to changes in concentration of the substance being titrated.

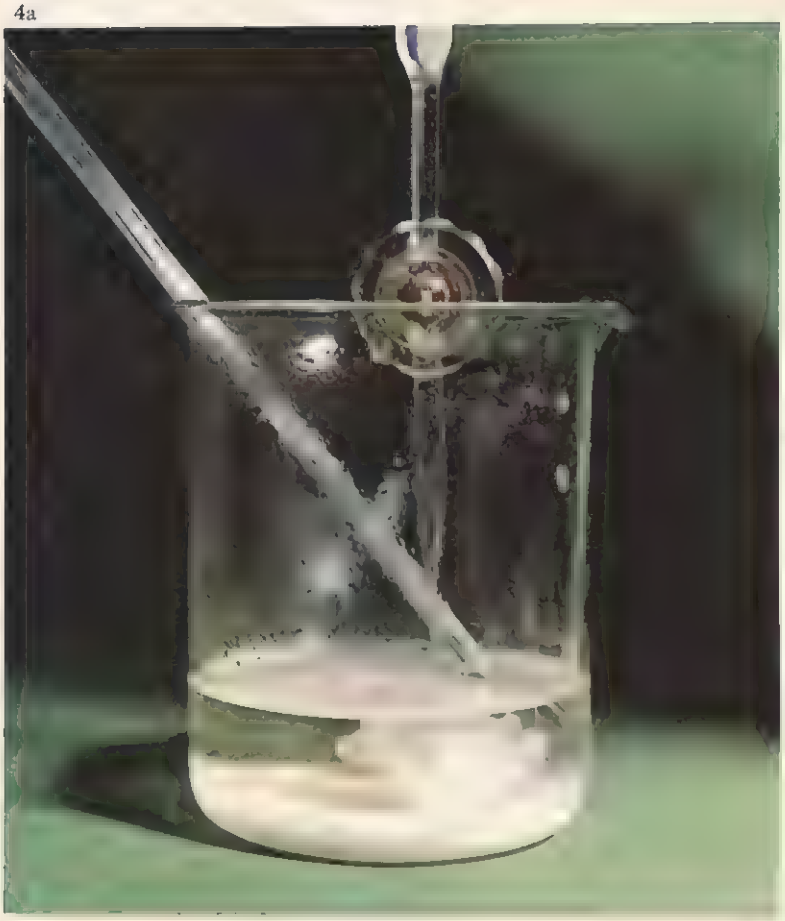
In conductometric titrations, a pair of electrodes, usually platinum sheets, is introduced into a titration vessel, and the electrical resistance is measured after the addition of successive portions of reagent. The reciprocal of the resistance, or con-

---

things, that on… …om of magnesium is present in eac… …e. Utilizing research of a different k… …nd that chlorophyll b consists of 4 pyrrole rings (**a, b, c, d**), each of which consists of 4 atoms of carbon (orange) and one atom of nitrogen (blue), joined by the bridge groups α, β, γ, and δ. A long paraffin chain is attached to carbon atom 7, and various radicals to the others.



4a



4b

**TITRATION**—One way of working out the titer, or concentration, of a solution (NaOH, for example) is as follows. Hydrochloric acid (HCl) at a known concentration (Illustration 4a) is added to the solution drop by drop from a graduated burette (a long glass tube with a tap). The base solution (which turns litmus paper blue) is gradually neutralized by the addition of the acid, yielding the salt NaCl (Illustration 4b). When the solution is completely neutralized, the litmus paper no longer changes color. Stoichiometric calculation is then used to work out the quantity of NaOH in the original solution.

ductance, is plotted against titration volume. Generally, the resulting graph consists of two straight lines intersecting at the end point.

Amperometric titrations are based on the measurement of electrolysis current during the course of a titration. The current is determined by the rate of supply of some substance to one of the electrodes. Because of this feature, the amperometric titration does not respond to the total conductance of the solution and the electrode response is therefore more specific.

In a coulometric titration the quantity of electricity required to carry out a known reaction is measured, and from Faraday's law, the quantity of material present is calculated. Coulometric titrations are customarily carried out either at constant potential or at constant current.

## OTHER USES OF STOICHIOMETRY

Stoichiometry is used whenever the weights of substances are to be calculated on the basis of a given formula. This means that the entire science of chemical reactions from the point of view of weight and volume makes use of stoichiometry. Stoichiometry is thus one of the foundation stones of industrial chemical processing and chemists are carefully trained in stoichiometric techniques. Processing plants are equipped with expensive regulating equipment to ensure that reacting substances are present in the correct proportions. In addition, stoichiometric calculations are extremely important to engineers in the evaluation of the performance of such equipment, as well as in the design of new equipment and in the modification of equipment already in use.

# GRAM-MOLECULAR WEIGHT | a key concept in chemistry

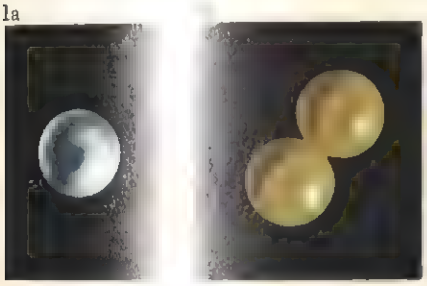
The molecule is the simplest of the combinations that occur between atoms of the same element hydrogen $H_2$, for example), or between atoms of different elements (hydrogen H and chlorine Cl, forming hydrogen chloride HCl, for example). Molecules may be monatomic (consisting of one atom), such as the neon (Ne) molecule, or diatomic, such as the chlorine ($Cl_2$) molecule, or tetratomic, such as the phosphorus ($P_4$) molecule, or octatomic, such as the sulfur ($S_8$) molecule, and so on.

Molecules are submicroscopic particles, too small for the human eye to perceive. Is it possible to weigh them? Despite the ingenuity of modern methods and techniques, the answer to this question is clearly no, not even with the most sensitive scales. It is possible, however, to assign molecules a relative weight value based on an arbitrary scale. This will not give the weight of a molecule in absolute terms, but it will yield the weight of a molecule with respect to other molecules. For example, the molecular weight of a molecule of oxygen ($O_2$) is 32.000, because the atomic weight of oxygen has been assigned a value of 16.000. Thus, molecular weight is no more and no less than the sum of the atomic weights of the atoms that make up the molecule. For another example, the molecular weight of the hydrogen chloride (HCl) molecule is 36.461, no more and no less than the sum of 1.008 and 35.453—the atomic weights of hydrogen and chlorine. Now, if 32.000. grams of oxygen is used in some experiment or other, this quantity is referred to as one "gram-molecular weight" of oxygen. In other words, whenever a gram quantity of a given substance numerically equal to the molecular weight of the substance is used, this quantity is called the gram-molecular weight. A gram-molecular weight of a substance is also called a mole of the substance. Multiples and fractions of a mole are also used; thus, 3.200 grams of oxygen equals 0.10 mole, and so forth.

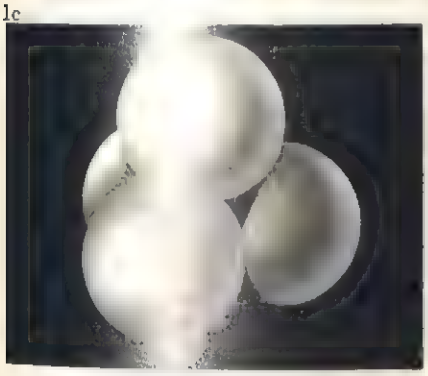
The gram-molecular weight is the molecular weight of a substance expressed in grams. It contains $6.02257 \times 10^{23}$ molecules. This number is known as Avogadro's constant. The weight of a single molecule can be determined by dividing the value of the gram-molecular weight by this number.

It is easy for modern chemists to say that the molecular weight of oxygen is 32.000, because the oxygen molecule consists of two atoms each with an atomic weight of 16.000. Suppose, however, that the structure of the oxygen molecule (or any other molecule) was not known. The French chemist Joseph Louis Gay-Lussac, working toward the beginning of the nineteenth century, made a careful study

1a

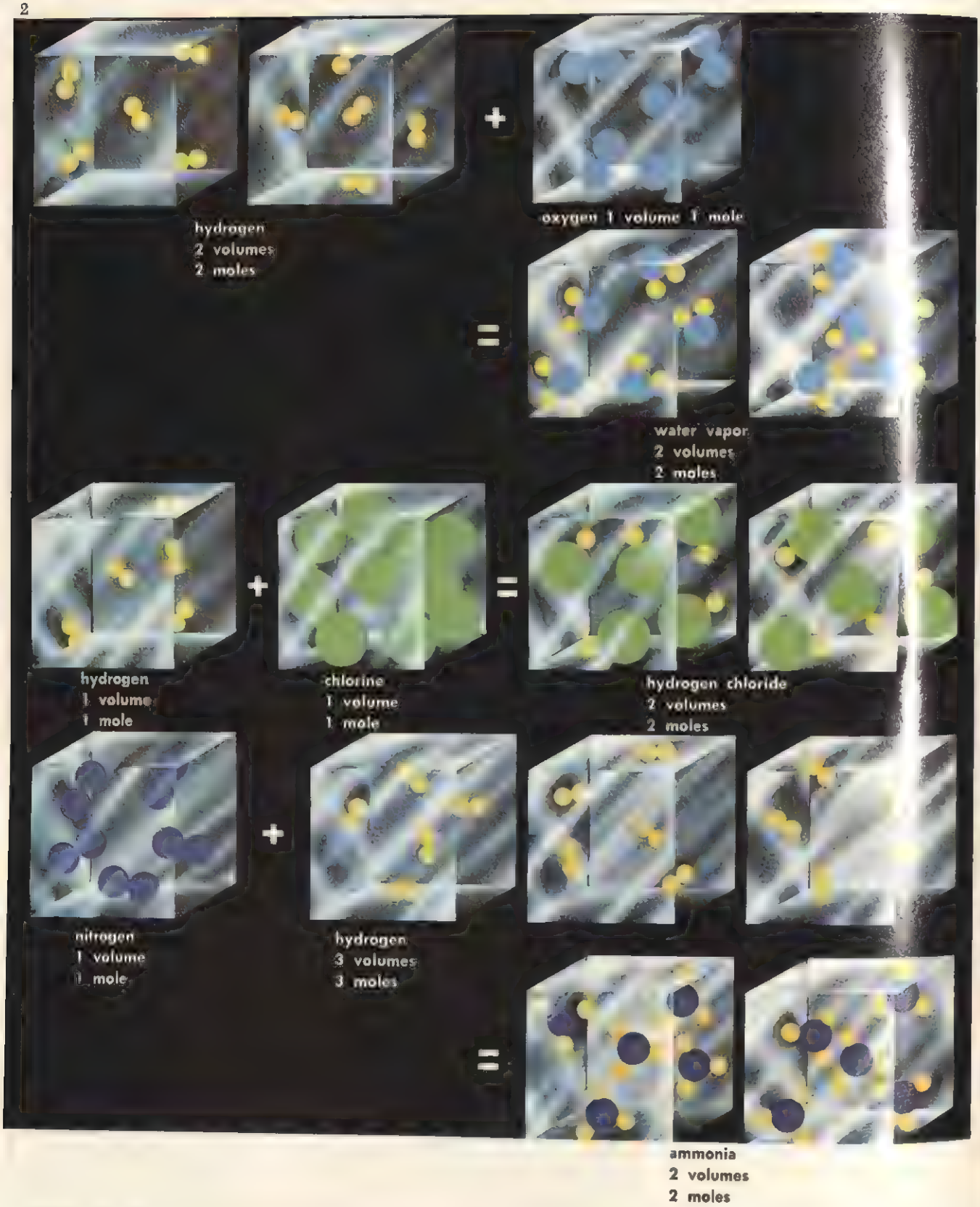


1c



**THE NUMBER OF ATOMS IN A MOLECULE**—The molecule of neon (illustration 1a) is monatomic—composed of only one atom. The hydrogen molecule (illustration 1b) is diatomic, or composed of two atoms. The molecule of phosphorus (illustration 1c) is tetratomic, with four atoms located at the vertices of a regular tetrahedron. Finally the molecule of sulfur (illustration 1d) is octatomic, with eight atoms arranged in a ring.

1d




**COMBINING RATIOS OF GASES** — Two liters of hydrogen combine with one liter of oxygen to form two liters of water vapor. One volume of hydrogen and one volume of chlorine produce two volumes of hydrogen chloride. One volume of nitrogen and three volumes of hydrogen produce two volumes of ammonia. These facts led Gay-Lussac to formulate his law: "The volumes of gases that combine with each other are in the ratios to each other of simple whole numbers; the same is true of the gaseous products." This led to Avogadro's law: "Equal volumes of different gases, measured at the same temperature and pressure, contain the same number of molecules. The molecules of the gases, whether reagents or reaction products, must have the same ratio as their respective volumes."

3

**MEYER'S APPARATUS**—When the glass rod **b** is removed, the solid substance **a** falls to the bottom of the test tube **c** where it is vaporized by the heat produced by boiling the liquid **d**. The vapor adds to the air in the system, which passes through the side tube **e**, enters the tube **f** upturned in basin **g**, and displaces the water in that tube. By measuring the volume of displaced air, which will be the same as the volume of the vaporized substance, and knowing the weight of the substance, its molecular weight can be calculated.

**THE DEEP BLUE OF THE SKY**—When no air is present, the sky is perfectly black. This is how astronauts see it. The air in the atmosphere diffuses the blue portion of the sun's light and causes the sky to appear blue. The higher the density of the air, the deeper the blue. Gauging the color of the sky can thus give an indication of the density of the air, if there is no haze or mist.

of the reactions that occur between gases. He noticed in particular that two liters of hydrogen react with a liter of oxygen to form two liters of water vapor:

$$2H_2 + O_2 \rightarrow 2H_2O.$$

Also, one liter of hydrogen combines with one liter of chlorine to produce two liters of hydrogen chloride:

$$H_2 + Cl_2 \rightarrow 2HCl.$$

Another Frenchman, the chemist Claude L. Berthollet, observed that three liters of hydrogen combine with one liter of nitrogen to produce two liters of ammonia:

$$3H_2 + N_2 \rightarrow 2NH_3.$$

Gay-Lussac used his experimental data to formulate a law that may be summarized as follows: When two gases combine, there is a simple ratio between the volumes of these gases and also between the total volume of the combined gases and the volume of the gaseous compound produced.

This law led to the conviction that equal volumes of gases, at the same temperature and pressure conditions, contain an equal number of particles, whether atoms or molecules. The result of all this was widespread confusion, since at that time the difference between atoms and molecules had not been clarified. The Italian chemist Amedeo Avogadro settled the controversy by changing the law to read: Equal volumes of different gases, at the same temperature and pressure conditions, contain an equal number of molecules. In practice, all that is required to calculate the molecular weights of gaseous substances (assuming Avogadro's law is true) is to weigh equal volumes of the substances. The result will be relative molecular weights. Avogadro's law also shows that a gram-molecular weight of any given gaseous substance, when at 0° C and a pressure of 1 atmosphere (standard temperature and pressure in other words), will always occupy the same volume. For example, if the volume occupied by each of three substances (a mole of oxygen, a mole of hydrogen, and a mole of nitrogen) is measured at 0° C and 1 atm pressure, the result is 22.4 liters in all three cases. To measure the molecular weight of a gas, therefore, it is only necessary to determine the weight at standard temperature and pressure of 22.4 liters of the gas.

To measure the volume of a solid, the substance must be converted to the gaseous state. For this Meyer's method can be used. This involves volatilizing a weighed quantity of the substance in an air-filled container, and collecting the air displaced. Since the weight of the substance placed in the container is known, and since its gaseous volume is equal to the volume of air displaced, the density of the gas in grams per liter and its molecular weight can be calculated. Since one mole occupies a volume of 22.4 liters (at standard conditions), the following ratio applies ($g$ = weight of the substance, and $MW$ = the unknown molecular weight): $g : V = MW : 22.4$. If $g$ grams occupy a volume of $V$ liters, the number of grams corresponding to the molecular weight $MW$ occupy a volume of 22.4 liters. The molecular weight is thus obtained from the equation:

$$MW = \frac{(g)\ (22.4)}{V}$$

($V$ is not precisely the volume read off in the graduated bell used to collect the air. Certain modifications not described here must be made.)

Avogadro's law met with considerable opposition at first. It is interesting to see how such confusion can arise. Suppose it is desired to find out the molecular weight of ammonium chloride ($NH_4Cl$), which is obtained by combining hydrogen chloride and ammonia ($NH_3$):

$$HCl + NH_3 \rightarrow NH_4Cl$$

Its molecular weight will obviously be the sum of the molecular weights of its components, that is, 53.5. If Meyer's method is used, however, the figure is reduced by about one half: 27. Why is this? After a lot of guesswork the idea was put forward that, due to the high temperature, the molecule of ammonium chloride had dissociated again into a molecule of hydrogen chloride and a molecule of ammonia. The volume occupied was thus doubled, and the apparent molecular weight halved.

## RELATIVE DENSITY OF GASES

The density of a substance is its weight per unit volume. In the case of solids and liquids, weight is expressed in grams and volume in cubic centimeters. In the case of gases, however, the liter is the best unit of measure for expressing volume. Gas density is thus expressed not in grams/cubic centimeter ($g/cm^3$) but rather in grams/liter ($g/l$). It is often useful to compare the density of a substance with the density of a standard substance. In the case of solids and liquids, the substance normally used for reference purposes is water. In the case of gases, it is usually hydrogen at standard conditions. The ratio between the density of the substance and the density of hydrogen is used to work out the molecular weight by means of the following equation:

$$D_1 : D_2 = MW_1 : MW_2,$$

where $D_1$ and $MW_1$ are the density and molecular weight of the unknown substance, and $D_2$ and $MW_2$ are the density and molecular weight of the standard gas. Measuring the densities of gases has frequently led to a determination of the structure of molecules.

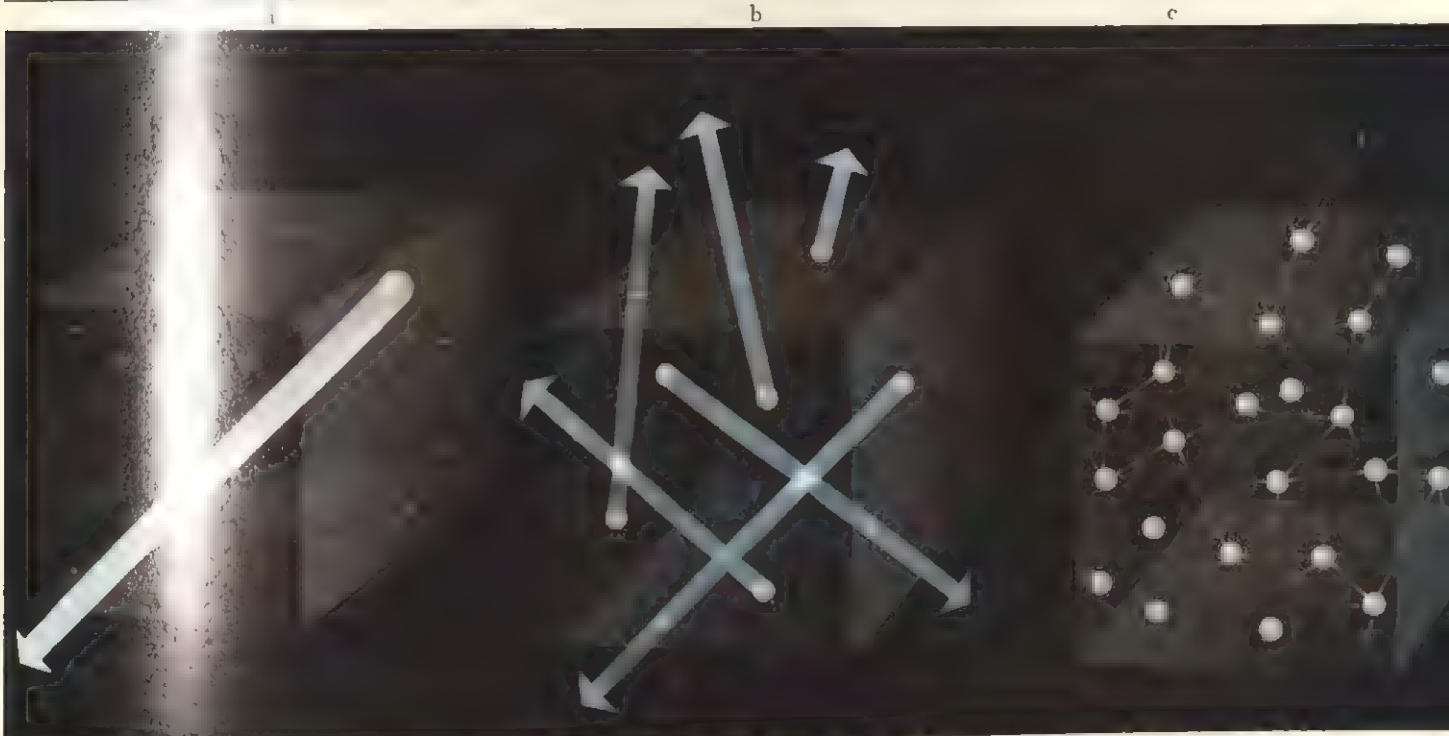
# THE MOVEMENT OF MOLECULES | continuous motion

Experimentation [illegible]eory are the keys with which mar[illegible]nlocked many of the secrets of th[illegible] of science. They have been the t[illegible] his study of the states of matter [illegible]ture of gases has made it simple[illegible]an to experiment and theorize w[illegible]more extensively than with liquid[illegible]s. Consequently, the knowledge[illegible]operties of gases is greater than[illegible] other forms of matter.

Fortunately [illegible] the theories that apply to gases [illegible]l in understanding liquids and [illegible]he kinetic theory, for example, t[illegible]about gases that is applicable to a certain extent to liquids and solids. According to the theory, gases consist of minute elastic particles, negligible in volume, that are always in motion and continually colliding with one another.

Among other facts known about gases are the average distance their molecules travel before colliding with one another and the existence of internal friction. Internal friction is determined experimentally, and theory serves to expand the concept. On the other hand, the average distance a molecule travels between collisions—its mean free path—can be worked out theoretically but is difficult to demonstrate experimentally. The mean free path of a gas, however, is useful in designing equipment to produce almost perfect vacuums, so that calculations based on the theory are of great importance in that application alone.

Many other characteristics of gases can be interpreted through the kinetic theory, such as the capacity of one gas to diffuse into another. Many facts about gases are evident from simple observation of their behavior, but theoretical calculation makes possible the prediction of the characteristic under examination.




**THE MEAN FREE PATH**—The average distance traveled by the molecules in a gas between two successive collisions is known as the mean free path. Between each two collisions, the molecules travel more or less along a straight line, at least in gases under normal conditions—a temperature of 20° C (68° F) and standard atmospheric pressure. The kinetic theory of gases allows the prediction of the mean free path of the molecules in a given volume of gas according to their size and density.

Assume that the gas molecules are perfectly spherical in form and that each moves in its own direction at an average velocity of $v$. Suppose the radius of the sphere of the molecule is known to be $r$. As a molecule moves along a straight line, it will sooner or later meet another molecule. The mean free path between molecular collisions may be calculated by considering the following equivalent situation. Suppose that initially only one molecule is moving at velocity $v$, while all the others are at rest (illustration 1a). Suppose, further, that this molecule has a radius twice as large as it actually has ($2r$ instead of $r$), and that all the molecules at rest have only the properties of points—that is, they are virtually without dimensions. In one second, this molecule will travel along a space that is cylindrical in form, with a base having the area of the sphere ($4\pi r^2$), and a length equal to the distance traveled in one second ($v$). The volume of this cylinder will therefore be $4\pi r^2 v$. The number of collisions to which the molecule will be subjected when traveling at velocity $v$ is equal to the number of molecules inside the cylinder, shown in illustration 1a as a light-colored path. In a volume $V$, which is defined as the volume occupied by one mole of gas under normal temperature and pressure, the number of molecules is equal to Avogadro's constant, $N$. A smaller volume will have a smaller number of molecules. The number of molecules encountered in a second by the traveling molecule will be

$$n = 4\pi r^2 v\, N/V,$$

where $N/V$ is the number of molecules present in the unit of volume.

On the other hand, when all the molecules are in motion (as actually occurs), the situation is more complex, as illustration 1b shows. The number of collisions is slightly greater than in the previous calculation and equals

$$4\sqrt{2}\,\pi r^2\, N/V.$$

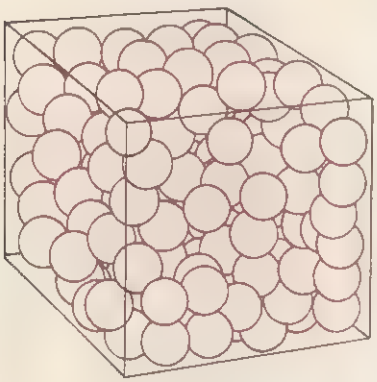
Now that the number of collisions that takes place per second is known, the mean free path (illustration 1c) can be calculated. In one second, the molecules travel over the distance $v$; therefore, if $n$ collisions take place in $v$, two successive collisions will take place at an average distance $l = v/n$. It can be said that the mean free path equals

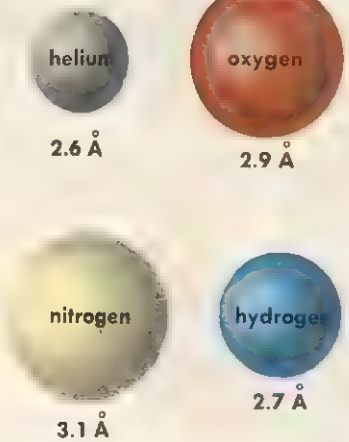
$$l = V/4\sqrt{2}\,\pi r^2 N.$$

2

**THE RADII OF MOLECULES**—To calculate quantities such as the mean free path of molecules and the number of collisions per second, it is necessary to know the radius of the molecules shown in Illustration 1a as spherical in form. Suppose that the molecules are practically in contact with each other in a liquid. One mole of a substance contains a number of molecules equal to Avogadro's constant. To find the volume of a molecule of oxygen, it is sufficient to measure the volume of 32 g (about 1.1 oz) of liquid oxygen: the volume of a single molecule of oxygen will be equal to this amount divided by Avogadro's constant.

By application, the characteristic data for the molecules of any liquefiable substance can be obtained. Illustration 2b illustrates the relative dimensions of molecules of oxygen, $O_2$; nitrogen, $N_2$; hydrogen, $H_2$; and helium, He. The diameters of the molecular spheres are shown in Ångstrom units ($1Å = 10^{-8}$ cm). Molecules of these elements are among the smallest of known molecules; those of many organic substances are much larger.






**THE MOLECULES OF AIR ENLARGED 10,000,000 TIMES**—Although for many reasons air cannot be considered a true gas, at normal temperatures it behaves very much like one. Illustration 3 shows a volume of air enlarged for the purpose of observing the molecules of a gas to scale. The cube as drawn has sides that measure 10 cm (about 4 in.). The cube represents a cube with sides measuring only 100 Å, or a hundred-thousandth of a millimeter, containing 30 molecules. Therefore, the scale of this diagram is 10,000,000 to 1. On this scale, each molecule of nitrogen and oxygen has a diameter of about 3 mm (about 0.1 in.), the equivalent of 3 Å (more precisely, 2.9 Å for oxygen and 3.1 Å for nitrogen). The average distance between molecules is about 25 Å. (This distance should not be confused with the mean free path, which is much longer.) The empty space between the molecules allows them to move freely. Between two collisions, each molecule travels an average of about 625 Å. On the scale of this illustration, this distance equals 62.5 cm (about 24.6 in.), a distance represented by the shortened arrow. Because the distance between the molecules is very great in comparison to their average diameter, they can travel for comparatively long distances before colliding. Nitrogen and oxygen travel, respectively as fast as 471 m and 440 m (about 1,545 and 1,444 ft) per second, or about 1 600 thousand-million times their diameters per second. Thus, the molecules shown at rest would not remain inside the cube, which measures 100 Å on each side, for longer than a fraction of a thousand-millionth of a second. This high velocity means that the molecules travel the mean free path in a very short time and thus are subject to collisions at extremely great frequency, causing them to change direction and velocity continually. The collision frequency, or the number of collisions that each molecule undergoes, is about 5 thousand million per second.

The data given here are valid for air under normal conditions—a temperature of 20° C (68° F) and a pressure of 760 mm (29.92 in.) Hg. If the temperature and pressure vary, these data also vary considerably. Lighter gases, such as hydrogen and helium, or heavier ones, such as the vapor of mercury, krypton, xenon, or radon, possess characteristics that differ somewhat from those of air.

3

**INTERNAL FRICTION** – A thin sheet of rigid matter moved through air will encounter a resistance because the object is forced to drag along those molecules of air that are in contact with its surface (illustration 4a). A sheet double the length of the first will encounter a doubly strong braking force. The braking effect is thus directly proportional to the area of the exposed surface. The molecules dragged through contact with the surface, in turn, drag the molecules of adjacent strata of air, causing friction.

In illustration 4b, the gas-filled space is divided into two strata that move in relation to each other. If the two strata were immobile, the molecules of the lower stratum would flow into the upper, following the vertical (red) arrows. Instead, because of the relative motion of the two strata, the molecules rise in the direction of the inclined (green) arrows, colliding in their turn with the molecules of the second stratum, moving the latter in the same direction, away from the vertical.

# BROWNIAN MOVEMENT



Many of the secrets of the physical world are invisible to the naked eye. These secrets are accessible, however, just as many of the mysteries of biology can be laid bare with an inexpensive microscope. Investigating molecules and atoms, however, is difficult. Nevertheless, it can be done, with patience, ability, and the desire to learn. This article describes a simple demonstration showing that matter consists of minute particles that are distinct from each other and in constant motion. Proof, indirect though it may be, of the existence of molecules is the purpose of the experiment described.

The equipment needed for this experiment is simple: a good microscope, two or three glass beakers, and a few substances stocked by paint dealers.

1

**MICROSCOPE PREPARATION** — All that is needed to observe Brownian movement is a suspension of minute particles in water. This can be prepared by mixing a small amount of varnish or any pigment (available from the local paint dealer) in a beaker or flask half full of water, as shown in the illustration. This suspension will immediately take on the color of the varnish or pigment, and will at first sight appear homogeneous; that is, the dispersed phase (the pigment) will be indistinguishable from the dispersing phase (the water). On the other hand, if the suspension is viewed through a microscope, it will be seen to consist of minute particles in constant motion. This motion is Brownian movement.

## A BOTANIST'S DISCOVERY

During the early part of the nineteenth century, the Scottish botanist Robert Brown was working with pollen, the male germ cells of flowers. Pollen is an extremely interesting substance to study. A grain of pollen consists of a small sphere covered with hairs. Striated markings on the pollen grain indicate the plant species to which it belongs. These minute grains range in size from a few hundredths of a millimeter in diameter (no thicker than a hair) to about a thousandth of a millimeter in diameter.

Using a microscope to observe pollen grains immersed in water, Brown discovered that the grains were in constant and irregular motion. Each grain was constantly changing position; moreover, the smaller the grain, the greater the distance covered between changes in direction.

Brown was unable to explain this motion. Scientists know today, however, that he was the first man to penetrate the frenetic world of molecules. This quivering of microscopic particles immersed in liquids is called Brownian movement in honor of its unknowing discoverer.

## MOLECULAR COLLISIONS

The atoms of solids, liquids, and gases are in constant motion. In the case of solids, the atoms or molecules are confined to certain positions in space, although they oscillate around these positions. The extent of these oscillations increases with temperature. In the case of liquids and gases, on the other hand, the atoms or molecules are free to change position throughout the entire mass of the substance. During this motion these particles naturally come into contact with other particles; the result is an enormous number of collisions. In the case of substances with low atomic or molecular weights, the speed with which the particles shift position may amount to hundreds of meters per second. This high speed partly explains why the movements of molecules cannot be followed directly. The other reason is that no optical microscope is powerful enough to bring molecules into focus. It is possible, however, to watch the effect of molecular collisions on particles somewhat larger than the molecules themselves. The particles being bombarded, of course, must be large enough to be seen through an optical microscope. This is done by immersing the particles in a gas or liquid.

Molecules do not all move at the same speed, although the average speed of the molecules of a given substance at a given temperature is more or less the same. Molecules of air, for example, move at a speed of about 500 m/sec (about 1,600 ft/sec). What happens, however, if a molecule of nitrogen, or of oxygen, collides with a particle of another substance such as cigarette smoke? The smoke particle, as a result of the collision, rebounds at a speed inversely proportional to its mass. Now, if a smoke particle has a mass ten million times that of a molecule of air, the molecule of air will come out of the collision at more or less its original speed. The smoke particle, however, will increase in speed by about 0.05 mm/sec (about 0.00 in./sec)—exactly one ten-millionth of the speed of the air molecule (oxygen or nitrogen). A particle this size is still too small to be seen through an optical microscope.

Assuming the smoke particle is composed of heavy atoms (like those of air) at a distance of about 3 Angstroms) from each other, it can be imagined as a cube whose sides are equal to $3 \cdot 3\sqrt{10{,}000{,}000} =$ about A. Since 1 A equals 0.0001 $\mu$m (mi), the particle has a diameter of at 0.065, or 1/16, of a micron. This puts it beyond the capacity of an ordinary optical microscope, although not an optical microscope equipped with a special device to be described later.

A small percentage of molecules move at a much higher speed (sometimes ten times higher) than the average. It may also happen that more than one molecule collides simultaneously and in the same direction with the smoke particle. The particle, if immersed in a gas, is thus surrounded by several thousand molecules, each of which collides with its neighbors, and sometimes with the intruding particle. About 5 billion collisions occur each second. Some of these collisions will obviously be more violent than others. This is why particles of the order of 0.001 mm (1 $\mu$m) or less demonstrate the existence of molecular movement.

a

b

**BROWNIAN MOVEMENT**—A drop of suspension is compressed between two microscope slides held in place at one end with a small amount of Canada balsam. The slide is mounted on a good microscope capable of enlarging 500 to 1,000 diameters. The slide must be illuminated sufficiently to make out all the grains in the suspension, but it must not be too bright. With practice the eye can make out increasingly smaller grains. The grains desired are the smallest of all (illustration 2a). These appear as green specks **a** on the light green background of the drop of liquid. The microscope is now focused on one of these grains (preferably in a group of other, larger grains **b** that can act as a point of reference). Instead of remaining stationary, the grain vibrates and moves around its position of equilibrium. (Sceptics will say the vibration is caused by movement of the laboratory bench. Prove that this is not so by observing the particle motion when the bench really is rocking).

Over a long period of observation, the particle will move in an irregular fashion. It will oscillate in all directions and at varying distances in a quite unpredictable manner. Illustration 2a, taken with a short exposure time, shows all the particles stopped in action. Illustration 2b, however, photographed under the same conditions but with a longer exposure time, demonstrates how the larger particles **b** appear sharp and clear because they were stationary during exposure. The smaller ones appear blurred because they were in motion. (1,500 X)

3

a

b

**AN IMPROVED METHOD OF OBSERVATION**—The microscopic observation method described above is the simplest from the point of view of the equipment needed. The result, however, is not as clear as it might be. The difficulty derives from the fact that molecular collisions in a liquid are much weaker than in a gas, and also that the particles are not much larger than the resolving power of the microscope.

This problem is solved by using an ultramicroscope. This device consists of an ordinary microscope equipped with an accessory that projects light onto the slide, but not into the microscope itself. The result is that the field of vision is completely dark. The light may be directed either from the side (illustration 3a), or from below (illustration 3b). When these light rays strike a particle (it may be smaller than even the smallest object visible as a shadow), the rays it deflects around itself enter the microscope's field. The particle, or the light scattered by it, therefore, becomes visible. This method reveals particles much smaller (and much more energetic in movement) than those visible by ordinary microscopic methods

Another refinement is observation of particles suspended in a gas. The molecules in a gas are much farther apart than in a liquid. This means that a particle of smoke, for example, covers much larger distances between collisions. The effect of the molecular collisions will, therefore, be much more obvious. For this kind of observation, however, expert skills in microscopy are required.

Far from being i…ctive, molecules—under normal circu…nces—are constantly in a state of one… of movement or another. Not only …tire molecules in a state of agitati… atoms making up the molecules …emselves, vibrating. Thus, when stu… nechanical models of molecules, i… l to keep in mind that a static a… nce belies a great deal of actual …

Mechanical … are useful tools for suggesting bon… es or distances between atoms. …rive at figures for these constant… ever, the vibration frequency or the rotational energy levels of the molecule must be calculated. This can be done with the aid of infrared spectroscopy.

As molecules vibrate, emissions or absorptions in the infrared range of the spectrum are created. These frequencies can be observed at wavelengths in the neighborhood of 10 $\mu$m (microns) with relatively simple and inexpensive equipment commonly found in laboratories. In fact, the radiations produced by molecular vibrations can be used as a means of chemical identification.

On the other hand, rotational energy and its rotation spectra require somewhat more sophisticated equipment for direct observation. These transitions are found in the microwave region of the spectrum, and the instruments for detecting them are often beyond the financial reach of the general laboratory. Fortunately, circumstances allow rotation spectra to combine with vibration spectra or electron transitions. Such conditions displace the more easily observable emission spectra toward the visible wavelengths to permit analysis by relatively simple means.

**VIBRATIONS IN …MIC AND POLYATOMIC MOLECULES**—A …ules are in motion to a certain extent …er they are diatomic (HCl and KBr, …mple) or polyatomic ($H_2O$, $H_2SO_4$, or …H, for example). While diatomic molecul… lining dissimilar atoms are easily studi… respect to emission spectra, molecul… taining more than two atoms (hence, n… in one bond) pose a slightly greater … However, if vibrating polyatomic mol… have a dipole moment —a physical … associated with the separation of … charge within the molecule—they … or absorb electromagnetic radia… milar to those of diatomic molecul… ddition, as a result of a polyatomic m… more complex structure, it can vib… a number of ways. As between diaton… ecules, the bond between two ato… tes in one way. However, because … eater number of atoms and bonds, a … tion of vibrations can exist.

These illustrat… beginning with a simple diatomic molec… progressing to more complex struct… how how increases in the number of … le vibrations are possible. The variou… s within molecules are represented by … eres whose sizes are roughly proport… to their atomic weight. Atomic movemen… thin the vibrating molecules is indicated by a set of arrows showing schematically the extent of each atom's motion.

Illustration 1a is a typical diatomic molecule in which the atoms are shown to move in opposite directions. In fact, this is the only type of vibration possible in such molecules. The motions of the atoms, or their displacements, are determined partially by their masses, the heavier atom moving in a shorter range than the lighter one. Note that the molecule's center of gravity remains unchanged even though the atoms are in constant motion.

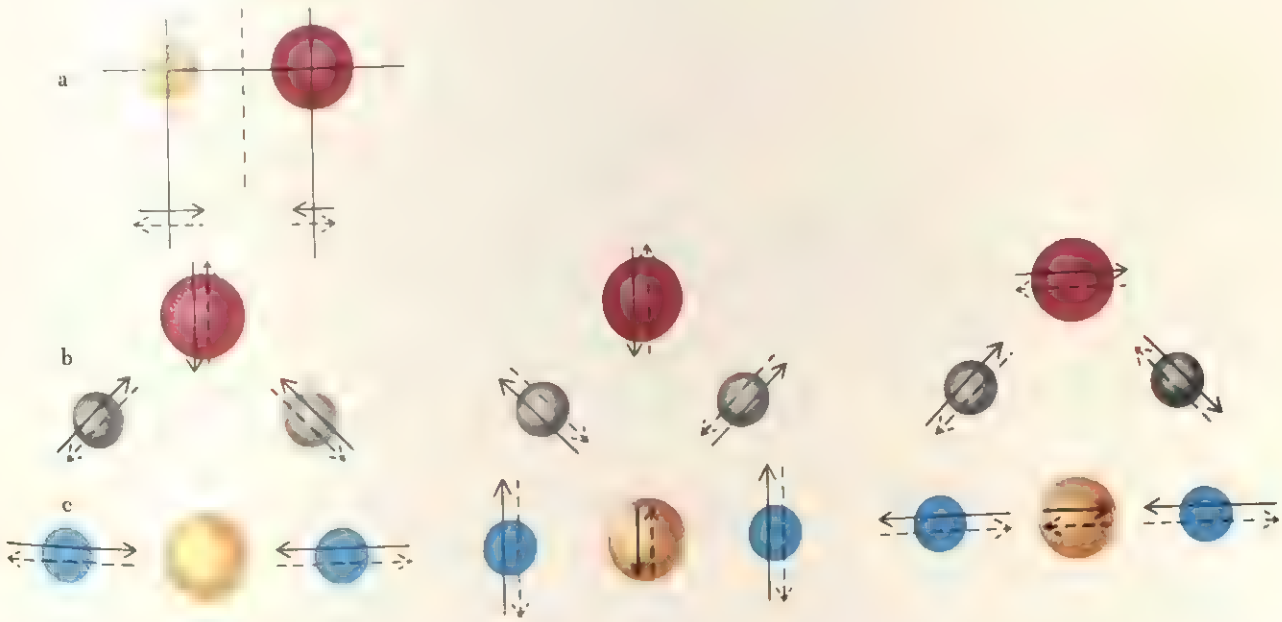
In a triatomic molecule such as that of water in the gaseous state, shown in illustration 1b, atomic motion becomes more complex. In a water molecule, the two hydrogen atoms and the single oxygen atom are linked in a manner that forms a bond angle of about 105°. Illustration 1b shows the different possibilities for atomic displacement in molecules of this type. In fact, the vibrations of a water molecule represent those observed in triatomic molecules of the $XY_2$ variety in which the individual atoms are not arranged in a straight line.

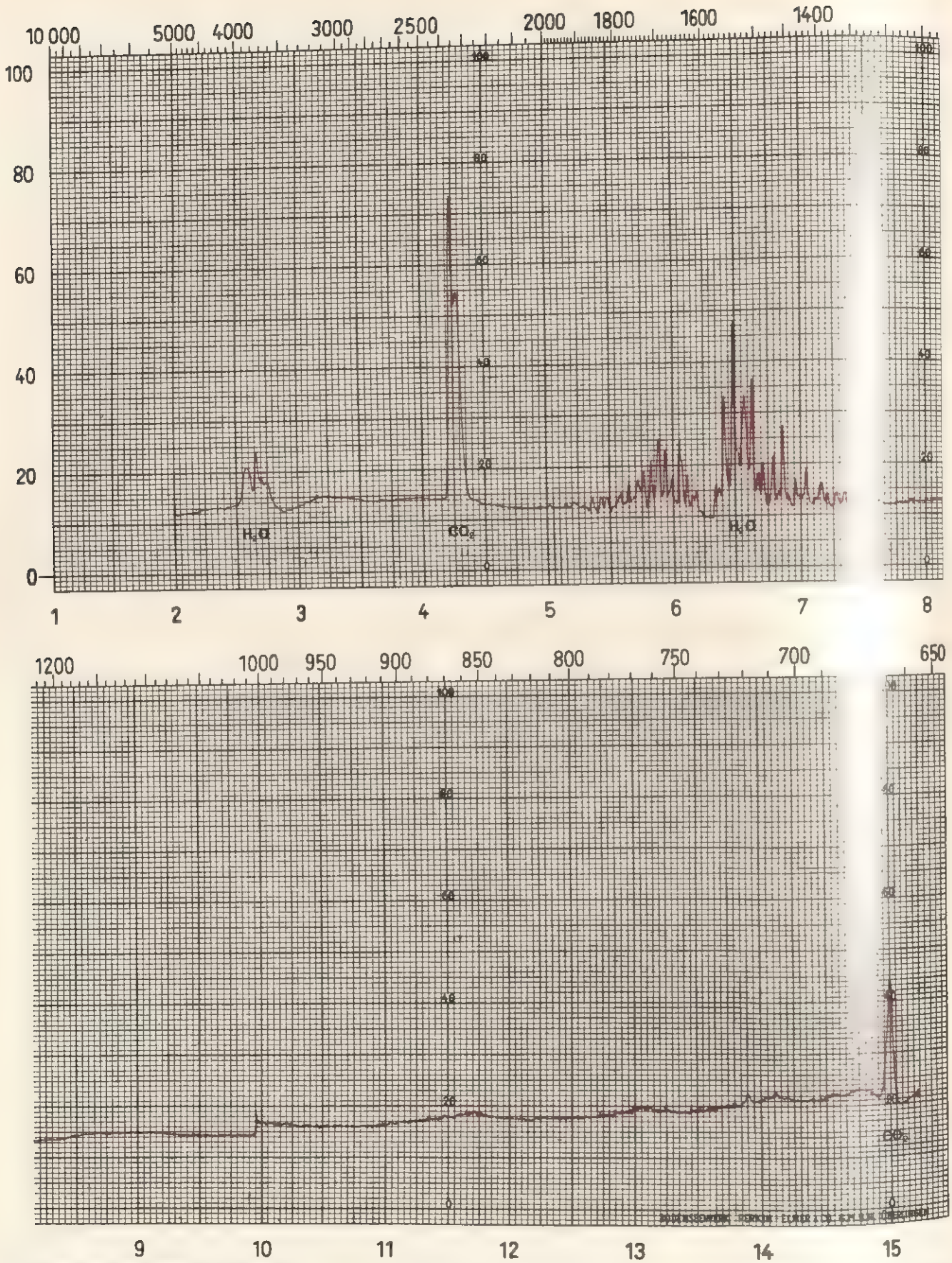
To indicate vibration frequency, scientists use a figure corresponding to the number of waves, or cycles, transmitted by a molecule within precise limits. In infrared spectroscopy, vibration is conveniently expressed as cycles per centimeter (or $cm^{-1}$), and from this the actual wavelength can be found simply by taking the reciprocal of the $cm^{-1}$ value.

In the case of the three water molecules in illustration 1b, the vibration frequencies in cycles per centimeter are, from left to right: 3,657.05, 1,595.00, and 3,775.79.

Carbon dioxide is an example of a linear $XY_2$ molecule, and is shown in illustration 1c. Here, it is represented by a carbon atom flanked by two oxygen atoms. The molecule's vibrations are the result of several causes: by an alternate lengthening and shortening (shown on the left), by deformation into a "V" shape (center), or by displacement of the atoms in opposite directions (right). In the first instance there is no variation of the electric moment caused by the vibration since there is no change in the molecule's center of gravity. Hence, there is neither emission nor absorption in the infrared range, and this frequency is said to be inactive in the infrared. However, combinations of this vibration with others have been observed, in which case the sum of the vibrations is manifested as a harmonic or combination of the other vibrations. In the second and third instances, the frequencies of the carbon dioxide molecule are 667.3 and 2,349.3 cycles per centimeter, respectively.

1

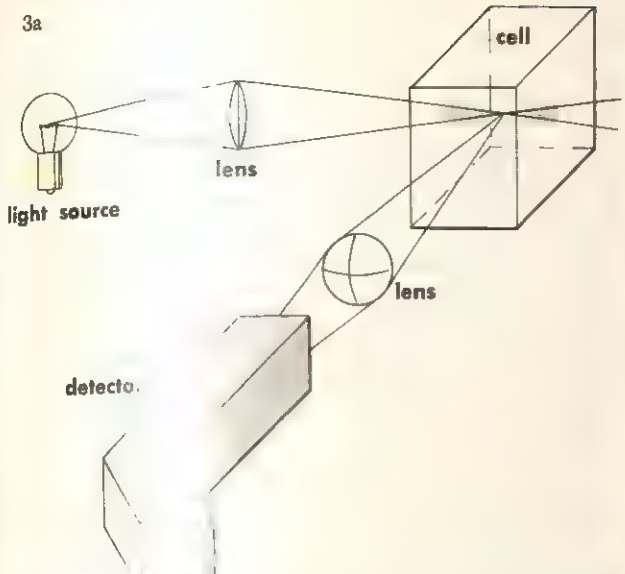





**CHARTED INFRARED VIBRATION SPECTRA**—To prepare readings of this type, infrared radiation is passed through a known volume of gas or liquid. A spectrophotometer capable of detecting the radiation enables visualization of the absorption bands caused by molecular vibrations.

The graph shown represents a recording of the infrared absorption bands of water (in the upper section) and carbon dioxide (seen in the lower portion of the graph). The tracing for water peaks at about 3,657 and 1,595 $cm^{-1}$, while the peaks for carbon dioxide occur around 2,349 and 667.3 $cm^{-1}$. In this graph, the scale at the bottom indicates wavelengths in microns with corresponding values in $cm^{-1}$ at the top. The percentage of absorption is indicated at the left. In the case of water, maximum absorption is in the neighborhood of 48 percent; in the case of carbon dioxide, maximum absorption is about 74 percent.

3a




3b

**THE RAMAN E**[illegible]-The combination of a vibrational (or [illegible]al) energy level and some other lev[illegible]isplace scattered light in a manner re[illegible]he vibrational (or rotational) transitio[illegible]s is the basis for the Raman effect, [illegible]menon that can be observed with ap[illegible]such as that shown in Illustration 3a [illegible]source provides radiation to a cell [illegible]g the substance under study, in this [illegible] water. The way in which the liq[illegible]scattered is observed through a dete[illegible]

The radiatio[illegible] through the water, or any substance [illegible]udied, is called excitation radiation. [illegible]tic amount, or quantum of radiation, st[illegible] electrons of the water molecules and [illegible]s diffused. Should such molecules be [illegible]te of minimum energy, the radiation n[illegible]luce no modification at all. In this cas[illegible]ult is normal scattering (Rayleigh scattering). If the particles of vapor are large enough, Tyndall scattering or diffusion can result. Smoke and fog, whose particles are of considerable dimension, provide good examples of such normal diffusion. Individual molecules may create the same effect, although with much less intensity.

While the eye can perceive the light that is laterally scattered by smoke, such is not true when pure water scatters light. Here, though there is a degree of normal scattering, there may also be anomalous scattering when the radiation causes molecular vibration or when the molecules lose energy by passing from one vibrational level to another. In the first case, the molecules absorb energy from the radiation, while in the second instance energy is emitted. In either circumstance, variations in energy always occur in specific amounts.

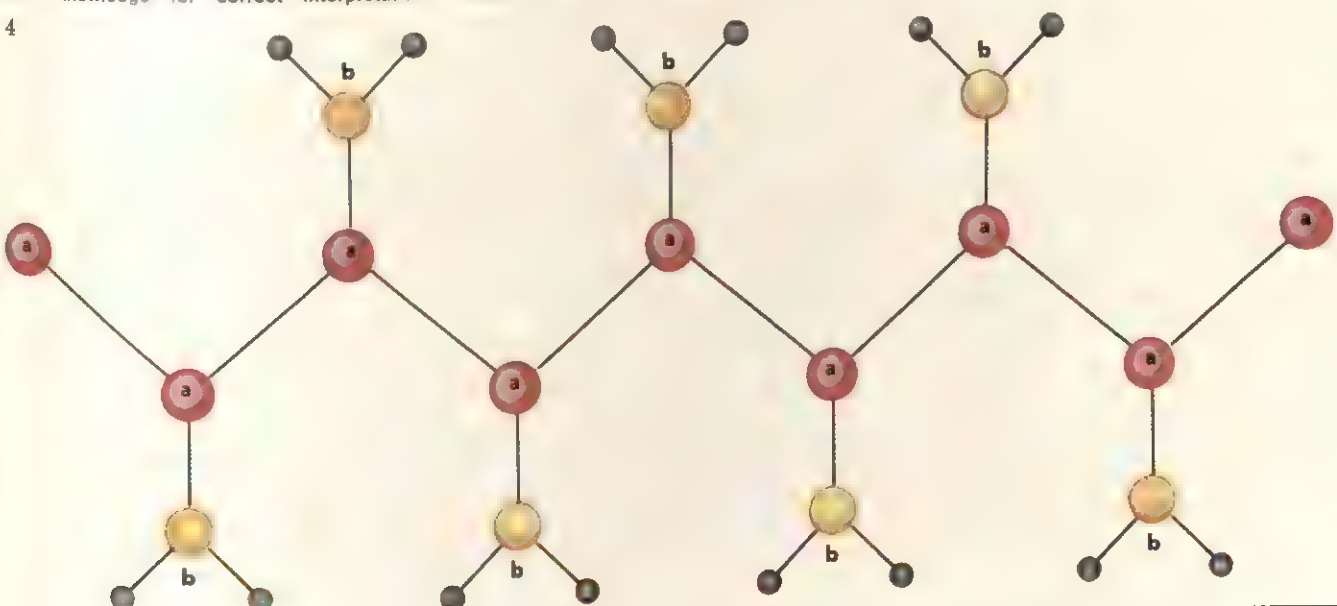
Illustration 3b is the scattering spectrum of pure water. The broad, intense line at the center is caused by diffusion without a corresponding modification in wavelength—the Rayleigh effect. On both sides, the equidistant and progressively weaker lines represent scattering in which the molecules have become excited or have lost energy. If lines of this type are to be clearly seen, a spectroscope with a bright optical system must be used. Exposures of the quality seen in this illustration often require sensitive film exposed for hours or perhaps days, or require the use of extremely intense sources such as a laser. The total picture represents the Raman effect.

The Raman effect makes possible the observation, using visible light, of transitions between vibrational energy levels. Until the advent of modern equipment, such as the infrared spectrometer, this research method was widely used.

**VIBRATIONS C**[illegible]**GE POLYATOMIC MOLECULES**—Just [illegible]mple molecules, a polyatomic configu[illegible]composed of many atoms in a chain can [illegible]ce observable vibrations. However, a mo[illegible] such as that represented here will vibrate [illegible] complicated manner that defies a simple [illegible]planation. The examination of such vibratio[illegible] spectra requires specialized knowledge for correct interpretation. However, by the study of mechanical models, information can be obtained that approximates data produced by sophisticated research (x-ray diffraction studies, for example).

From the illustration, it is obvious that if an atom **a** in the center of the chain vibrates, a large number of other atoms will also be caused to vibrate. On the other hand, the atoms making up a radical **b** can vibrate almost as freely as though they were isolated molecules. Thus, the vibration frequencies of the radicals can be studied separately. Knowing the vibration frequency of the principal chain, and combining this with what can be learned from the groups linked to the chain, a composite picture of the entire molecule can be achieved.

4

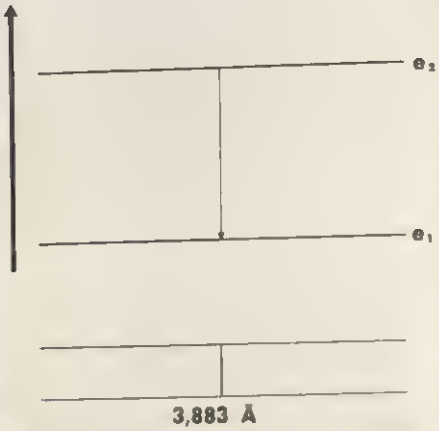


# DIATOMIC MOLECULES | vibrational and rotational states

1

a

b




**ELECTRON TRANSITIONS IN CN RADICALS IN THE FLAME OF AN ARC**—Illustration 1a shows the flame of a carbon arc. The outermost part of the flame contains unstable CN particles. These particles are produced when the carbon of the electrodes comes into contact with atmospheric nitrogen. CN radicals decompose at ordinary temperatures. This carbon arc served as the source for all of the spectra shown in this article. The CN spectrum of the sun is produced in a manner analogous to what happens in the carbon arc. (The CN band of the sun, howev[illegible]iffers in appearance from the spectra [illegible] in this article because it is produced [illegible]orption.)

The plasma of a carb[illegible] contains many molecular fragments—s[illegible]ng on the order of billions of billions. Th[illegible] particles collide violently with each othe[illegible]d with the molecules of the gas in whic[illegible]e arc is set up. Such collisions are su[illegible]ly energetic to excite molecules to hi[illegible]ergy states. Excited electrons attain [illegible]r energy level and then return to the [illegible] energy level in a very brief space of [illegible]n the order of $10^{-8}$ seconds). The fal[illegible]e electron from a higher to a lower e[illegible] level is accompanied by emission of e[illegible]romagnetic radiation. Suppose for the mo[illegible]nt, however, that the CN radical neither vi[illegible]es nor rotates. In this case all of the part[illegible] excited by collisions will emit the same [illegible]ochromatic radiation (a wavelength of ab[illegible] 3,883 Å). Illustration 1b shows the two en[illegible]y levels $e_1$ and $e_2$ that correspond to the [illegible]tates of the CN radical; that is, after t[illegible]ng collision and after the release of e[illegible]he lower part of the illustration show[illegible]pectral line that corresponds to this t[illegible] from the higher level $e_2$ to the lower le[illegible]

Spectrum analysis leads to the structural and mechanical characteristics of diatomic molecules; that is, to the internal movements that are possible by the two atoms within a diatomic molecule. The results of such analyses can then be applied to polyatomic molecules—molecules that consist of more than two atoms.

A diatomic molecule behaves somewhat like a vibrating rotor; that is, like a pair of heavy point-sized masses that vibrate while they rotate. Such a particle can emit vibrational and rotational energy in the form of electromagnetic quanta. The energies of these quanta depend on the initial and final energy states of the emitting molecule. Not all energy transitions are possible—only those permitted by specific rules.

The characteristic spectrum of each molecule is determined by the energies of the various levels and the selection rules governing transitions between the levels.

Study of rotational or vibrational spectra in diatomic molecules presents a number of difficulties because the radiation emitted falls within ranges of wavelengths not easily explored—the near and middle infrared in the case of vibrational spectra, and the farther infrared or the microwave range in the case of rotational spectra. The task of analysis can also be accomplished when the molecule undergoes a vibrational or rotational transition at the same time it undergoes an electronic transition; that is, at the same time that it emits a photon. Another method uses the loss or gain of a quantum of energy in a light beam. This is known as the Raman effect; it is used to determine the vibrational spectrum of a molecule. The other example is that of the complex spectrum associated with excited molecules at high temperatures.

An electron of an atom within a diatomic molecule may change its energy level inside the molecule. This is the case for the electrons of a hydrogen atom free to move about in space and not subject to the action of any external force. If the electron undergoes an energy level change in an atom that is bound to other atoms within a molecule, then the energy levels will no longer be the same as they would be if the atom were free. The energy jumps that an electron may undergo inside a molecule, however, are just as great as tho[illegible]t take place in an atom. The radi[illegible]mitted during such energy transit[illegible]lls within the range of visible ligh[illegible]n 4,000 to 7,000 Angstroms), or wit[illegible] the near ultraviolet region.

In the Raman eff[illegible]e molecule absorbs or emits a pa[illegible]ts rotational or vibrational energy u[illegible]nteracting with a beam of visible or [illegible]iolet radiation. In this case the rotat[illegible] and vibrational spectra appear as v[illegible] and ultraviolet radiations. Instrum[illegible]f great resolving power make it [illegible]ible to measure wavelengths with g[illegible]accuracy. Thus, it is possible to lear[illegible]great deal about the mechanical cha[illegible]teristics of diatomic molecules

The electronic spectra of diatomic molecules exhibit lines found in the spectra of many natural sources, particularly sources of interest to astronomers. Thus, the effect of absorption of oxygen molecules can be observed in the terrestrial atmosphere. These molecules produce spectral lines grouped into bands (just as for all other spectra of diatomic molecules) in the near infrared. The sun's spectrum contains bands of other mole-

cules (or rather licals), such as CN, CH, and $C_2$, but se are found in the ultraviolet regio

Other stars e pectra due to more complex molecu ven comets produce spectral lines t eal the presence of molecules. The intense line is due to the CN radical. In some stars it is even possible to record the spectrum of molecular carbon, and to determine the ratio between the various carbon isotopes. These isotopes give rise to similar and overlapping spectra with lines of different intensities. Intensities vary in proportion to the abundance of the isotopes.

The rotational and vibrational spectra of the diatomic radical CN are significant. The spectra shown can be obtained easily. It is necessary only to set up a carbon arc; the spectrum of the CN radical will be produced in the flame of the arc.

2

**FINE VIBRATION** **RUCTURE**—The actual spectrum of CN iewhat more complex than the one just ed. This is so because the energy emitt le the electron goes from the higher lower energy level is augmented by ltaneous liberation of vibrational energy. In other words, a molecule experiencing a collision increases its vibrational energy. This is quite distinct from the excitation of an electron to a higher energy level. Later, when the electron degenerates and liberates energy in the form of electromagnetic radiation, the vibrational energy also decreases. Because the two energies are additive, the molecule emits a photon whose energy does not correspond to the electron transition alone. The energy is greater; it corresponds to the sum of the electron energy and the vibrational energy.

Illustration 2a shows the electron energy levels of the CN radical. At each electron energy level there is a series of vibrational energy levels.

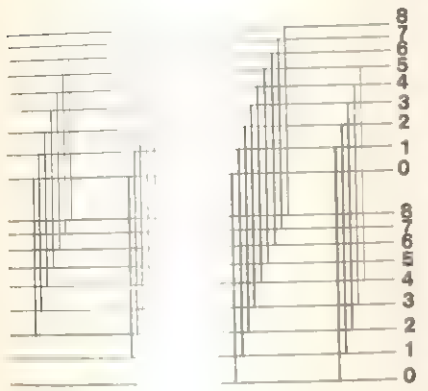
A transition may occur between the 0 state of one level and the 0 state of a lower level; this is the case shown in Illustration 1. In fact, this electron transition is the most probable one, at least under the conditions of the carbon arc. In actuality, there are also transitions between vibrational state 1 and the vibrational state 1 of the adjacent level. In this case the energy liberated is somewhat greater than in the previous case. This means that the vibrational levels in the excited electron state are farther apart than they are in the lower level of electron excitation. Similar and even more pronounced increases of energy can be noted in the transitions 2-2, 3-3, and so on.

A particular spectral line corresponds to each of these transitions, as shown in Illustration 2b (the illustration also shows the transitions that occur between other pairs of levels). The total of these lines gives rise to the rather complex spectrum shown here in schematic form. Note at the center the transition 0-0 just described. Lines corresponding to transitions that involve changes of vibrational levels are found to the left and right. Each group of lines is called a vibrational band. The lines in such a band are either almost equidistant or tend to move closer together in a particular direction. In the lower part of the diagram the lines are developed into a pattern of columns and lines. Each horizontal line of the table represents the spectral lines generated by the same starting level. The inclined dotted lines show that the spectral lines that have a common finishing level have their centers aligned.

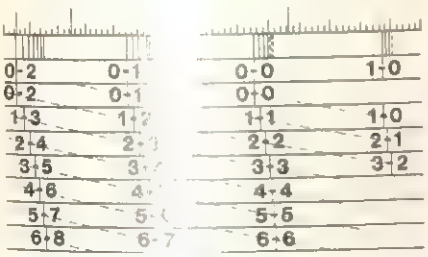
Illustration 2c shows the CN spectrum as it appears in the carbon arc. This particular spectrum was obtained by means of a spectrograph with weak dispersion capacity and a low resolving power. The lines corresponding to the various vibrational transitions are thus rather close together. The numbers of the vibrational levels of the radical between which the transitions occur are shown at the top. The lines corresponding to the different transitions differ in intensity. Thus, several different spectra taken with different exposure times have been superimposed. The very intense lines can be seen clearly in the spectra taken with short exposure times (bottom strips), while the weak ones are seen more clearly in the spectra where the exposure was long (top strips). At the left of the spectrum, which appears lighter and corresponds to the red part, are some groups of lines that are due to the analogous vibrational structure of an electron transition in a $C_2$ molecule.

If the structure of the spectrum is studied very carefully, the lines under consideration are seen not to have a perfectly symmetric form, but rather tend to fade away. Given the characteristics of the spectrograph used, this fading is due to CN rotational transitions that become superimposed on the vibrational transitions.

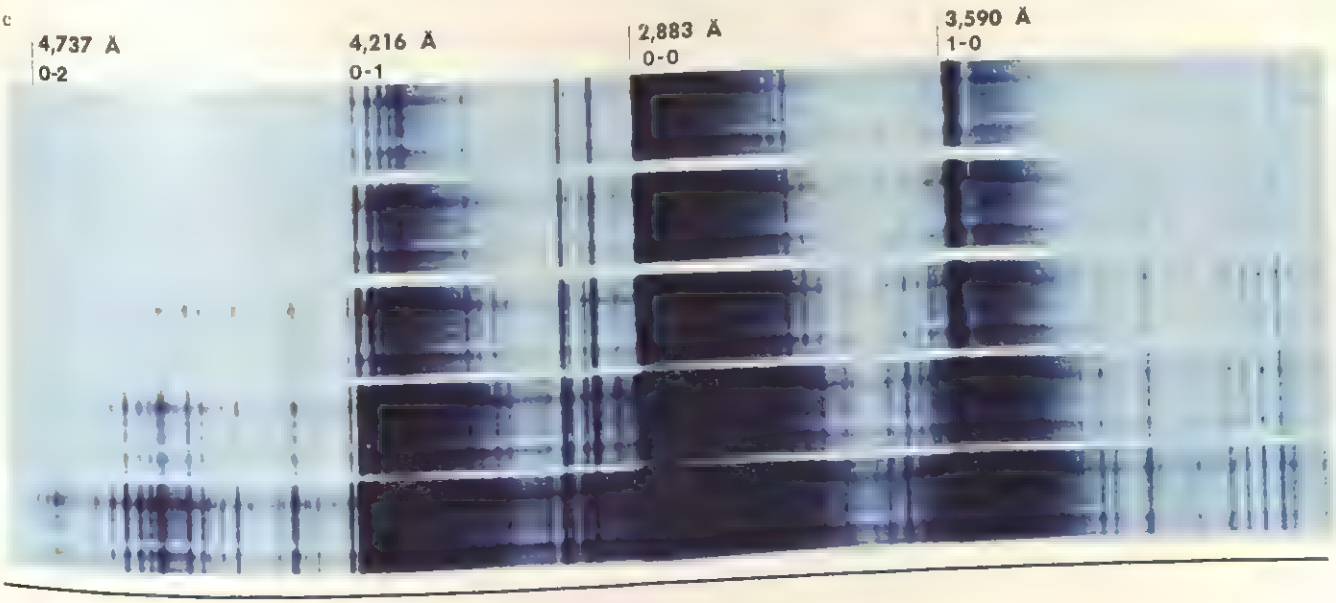
a

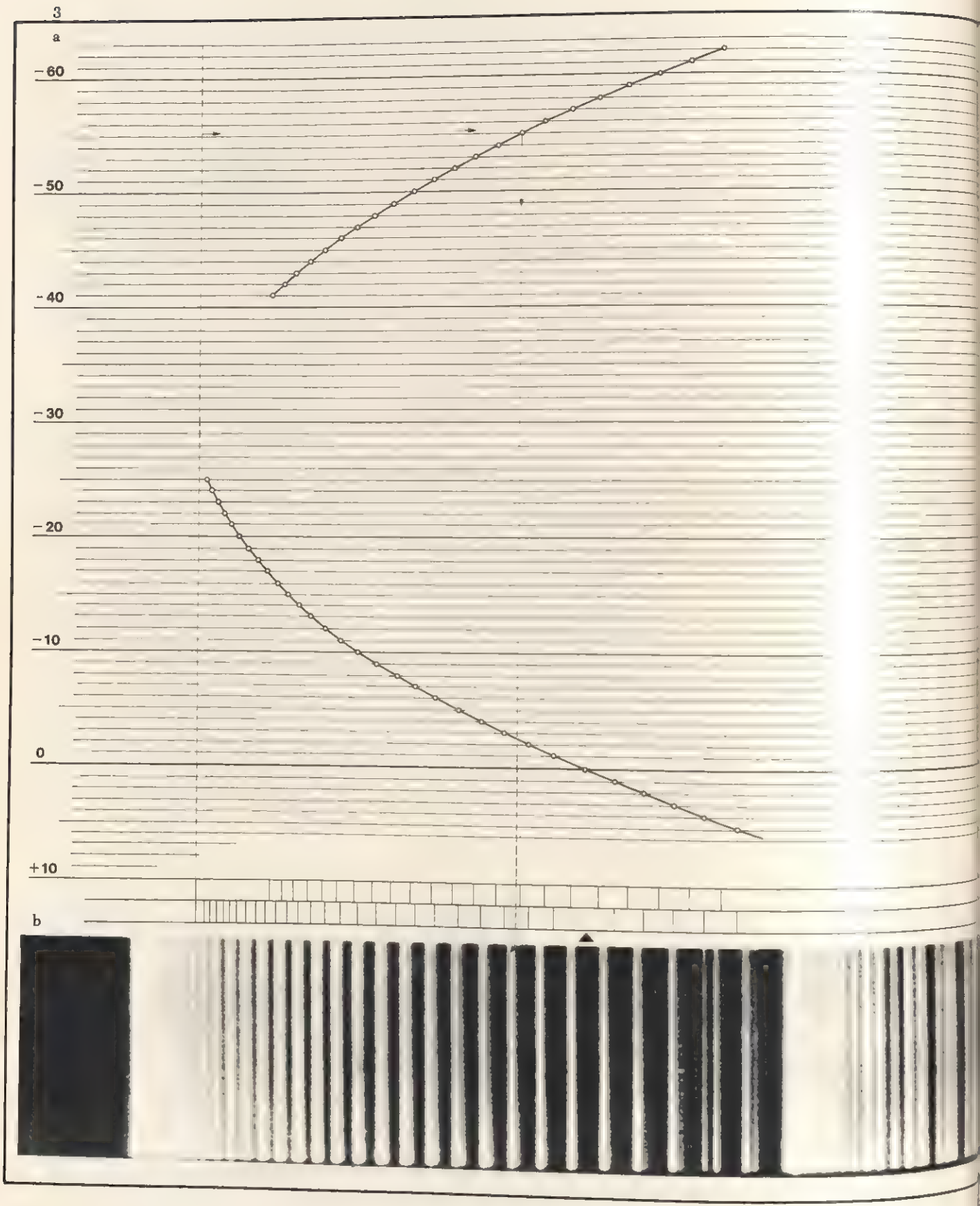



b

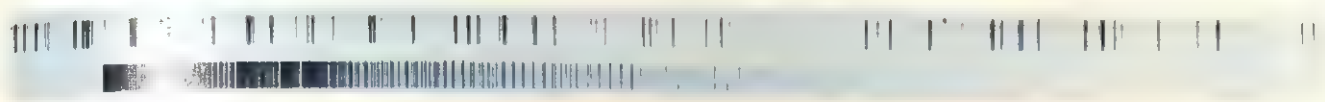



c

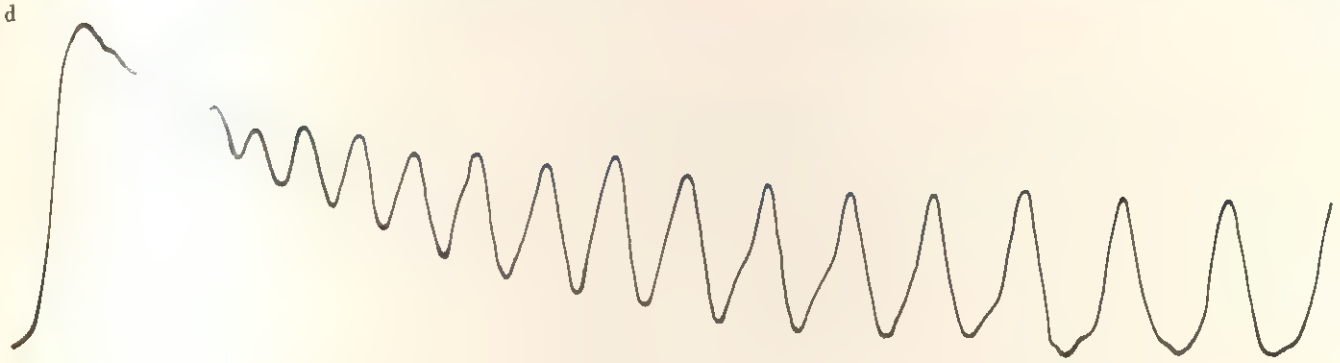



3
a
−60
−50
−40
−30
−20
−10
0
+10
b

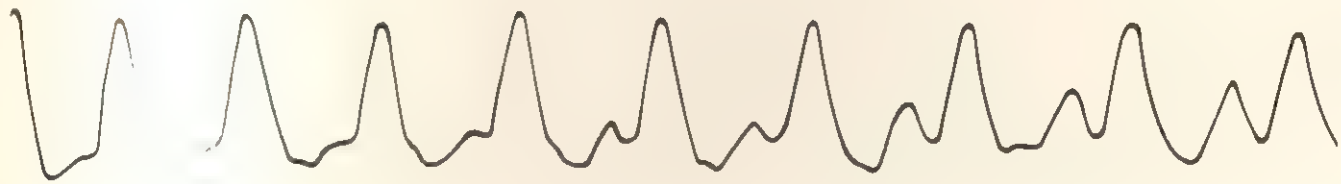
c



d



d′



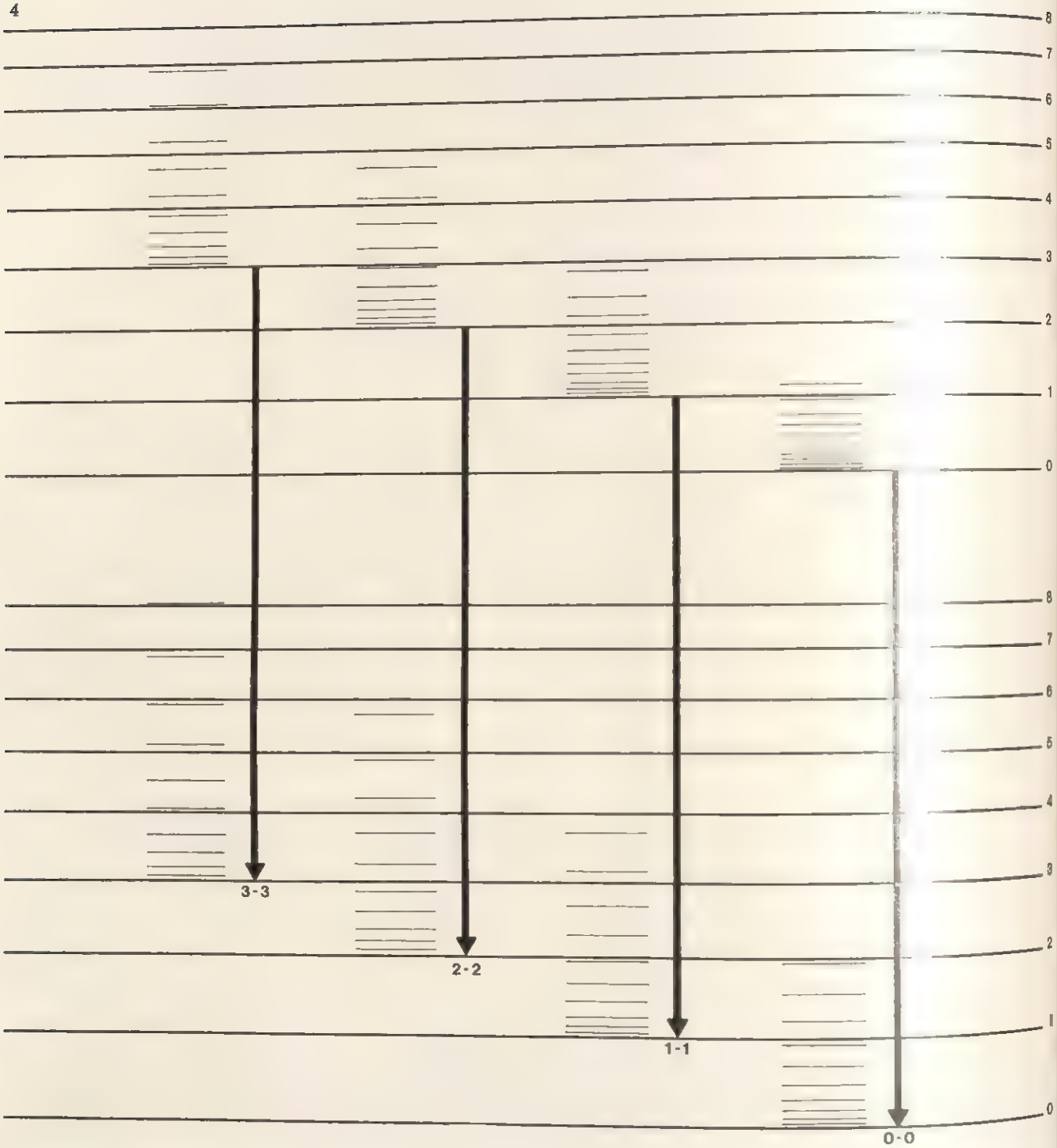
**ANALYSIS OF V IONAL SPECTRA**—Illustration 3c show portion of the spectrum previously show ustration 2c—more precisely, the regi ound 3,883 Å. This spectrum is now gr enlarged along the horizontal because it is obtained by means of a more sophistica spectrograph. The lines corresponding to the vibrational transitions between the two electronic levels characterized by the symbols 0–0, 1–1, 2–2, etc., are clearly visible. The lines in illustration 2c appear to fade because each line was really a band of lines.

Illustration 3b shows the details of a rotational band. The band shown here is the spectral region around 3,883 Å. By virtue of the very great enlargement (the horizontal scale is about 1 Å/cm) the lines corresponding to the various rotational transitions are quite distinct. The graph plotted above (illustration 4a) shows the number on the *y* axis that corresponds to the rotational level, while the *x* axis shows the position of the corresponding spectral line. For example, −55 on the *y* axis corresponds to a very intense line in the spectrum below the graph.

A second vibrational band is located to the right of the spectrum. This is the band adjacent to the one at 3,883 Å. Its lines are superimposed on the lines of the previous band, which are already very widely spaced at this point. It is interesting to note that the lines of the band are not all equally intense. The intensity of the lines diminishes as they approach the point at which variation of the rotational level is zero. In fact, the line at this point is missing. An arrow shows where it ought to be. Note also that the arrangement of the lines in the band gives rise to a perfectly parabolic curve (illustration 3a).

Curves such as this can be constructed for each of the bands observed in the spectrum. These curves permit the derivation of interesting information about the structure of a molecule. For example, it is possible to deduce a molecule's dimensions in the two electronic levels, and in each of the vibrational levels. It is also possible to determine the moments of inertia the molecule assumes in the various vibrational levels. It is, therefore, possible to predict molecular elongation as the vibration becomes more intense. An accurate plotting of the curve of the Morse potential that characterizes the molecule is also possible.

If an accurate analysis of the positions of the lines is desired, the spectrum is passed through a microphotometer. This produces the traces shown in illustration 3d and 3d′. The exact positions of the spectral lines can then be measured on these traces, giving the correct values for their wavelengths and/or frequencies.




**ROTATIONAL STRUCTURE**—The structure of a molecular spectrum is far more complex than the one just described. In fact, to explain the fading of the lines observed in the previous illustration, it is necessary to include molecular rotation.

This illustration shows how the energy levels of each electron state are complicated by molecular rotation. For the sake of simplicity, however, this diagram shows only the rotational structure of the vibrational levels corresponding to vibrational transitions 0–0, 1–1, 2–2, and 3–3. The CN radical is not a rigid rotating body. Thus, each vibrational energy level has a corresponding level position different from the others. For this reason, the transitions between all the possible rotational levels of one vibrational level and the corresponding ones for the other electronic levels do not produce lines of the same wavelength.

# DETERMINATION OF MOLECULAR WEIGHT | a volumetric experiment

Early chemists ... or later had to approach the pr... of measuring the weights of th... idual molecules of which matter ... de up. Such a prospect of delving ... e invisible molecular world may ... en filled with emotion bordering ... repidation. Without the benefit of ... isticated equipment and technical e... se, it is not difficult to understand ... probability of their concern.

Today, det... ion of molecular weights is a ... nplace occurrence employing me... known to even the neophyte chem... with such elaborate equipment as ... ass spectrograph, a great number ... lecular weight measurements can ... le in a short time—measurements ... fantastic precision. Even given th... hat most laboratories are not equ... with this apparatus, reasonably ac... measurements are possible using ... pler instruments.

## EXPERIMEN... DETERMINA... OF MOLECU... WEIGHT

One method o... lating the molecular weight of a s... nce uses techniques from both chem... and physics, and is not inordinate... fficult. It should be noted, however, ... t the values obtained from this method ... e not utterly precise. The purposes of this description do provide insight into the techniques for making such determinations.

By definition, molecular weight is simply the weight of a single molecule of matter expressed in relation to a reference unit. The reference unit used today is equal to one-twelfth the weight of the carbon-12 isotope, and for practical purposes this is considered to be a constant 1. (In the past, hydrogen was used as the basis for comparison. The field of nuclear physics has demonstrated carbon-12 to yield more accurate measurements, however.) Thus, to state that the molecular weight of water is 18 simply means that a water molecule weighs 18 times as much as the carbon-12 reference unit. In practice, scientists do not deal with pounds or ounces, but with a quantitative unit called the gram molecule, or gram mole. This unit represents that quantity of a substance whose mass expressed in grams is numerically equal to its molecular weight. Therefore, since the molecular weight of water is 18, this same figure constitutes a gram mole of water.

From the laws concerning perfect gases, it is known that a gram molecule of any substance in the gaseous state occupies a volume equal to 22.414 l (liters) at standard atmospheric temperature and pressure (0° C and 760 mm of mercury). The molecular weight of a substance can, therefore, be determined by measurement of the volume that a given weight (in grams) of the substance in gaseous form occupies at standard temperature and pressure. For example, 1 g of gaseous water occupies 1.2452 l at standard temperature and pressure. For the same substance to occupy 22.414 l, 18 g are required and this figure represents a gram mole of water, which, in turn, is the molecular weight of water.

## THE EXPERIMENT

There are several ways in which the molecular weight of a material can be found experimentally, and these depend on the nature of the substance. Some methods are particularly suited to measurements of gases, while others are applicable to solid but volatile matter, and still others to substances that are only slightly volatile. The experiment described here is based on an idea developed by the French chemist Joseph Louis Gay-Lussac in the nineteenth century.

The substance chosen for analysis for this experiment is the simple organic compound, ethyl alcohol, $CH_3CH_2OH$, a highly volatile liquid with a molecular weight of 46.07. At standard temperature and pressure, a gram mole of vaporized ethyl alcohol occupies 22.414 l—a considerable volume. For practical purposes, only 1 g of the alcohol is used and this will require a bit less than 0.5 l of space when vaporized. Thus, the container for collecting the gaseous alcohol must have at least a 500 ml capacity. For this purpose, a 500 ml graduate serves admirably, although a graduate of greater capacity could be recommended to facilitate the taking of readings and to make provision for error.

The causes of errors and the methods for correction are concerns for any analytical experiment. Those endemic to the determination of ethyl alcohol's molecular weight in the experiment under consideration are:

1. Inaccuracy in weighing the sample. One gram of liquid ethyl alcohol is approximately equal to 1.03 $cm^3$. However, volumetric measurement with a syringe requires utmost precision, so that complete accuracy cannot be assumed without the use of an analytical balance.

2. A marked inaccuracy can occur when the volume reading of the vaporized alcohol is taken because all of the air in the system may not be forced out.

3. Water vapor cannot be totally eliminated from the graduated measuring cylinder, and this water vapor occupies a certain amount of space.

Errors can be corrected to some extent by using calculations from tables of physical constants. For example, a well-established relationship exists between partial pressure of water vapor and temperature. As indicated in the following table, increased temperature leads to a greater partial pressure:

| | |
|---|---|
| 15° C | 12.788 |
| 16° C | 13.634 |
| 17° C | 14.530 |
| 18° C | 15.477 |
| 19° C | 16.477 |
| 20° C | 17.535 |

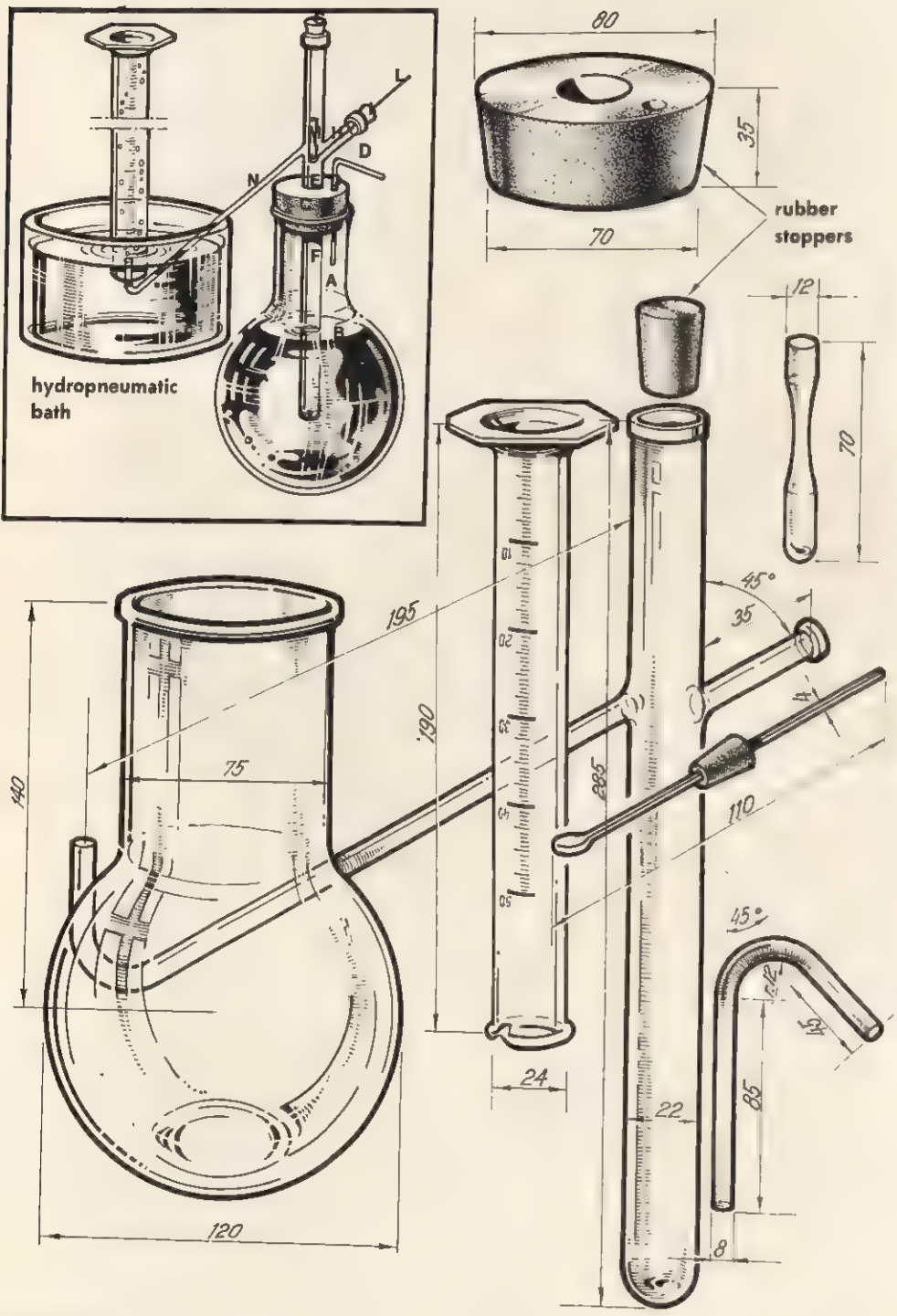



**DIAGRAM OF THE APPARATUS**—Although this illustration details the components of the apparatus required to determine the molecular weight of ethyl alcohol, it shows how they can be made, all the items described are commercially available. How the construction of the components can be a rewarding part of the experiment. The dimensions are given in millimeters.

The insert at the upper left shows how the components are put together. The heat-resistant flask **A** is partially filled with water **B** and capped with a two-hole rubber stopper **C**. The small tube **D** provides a vent when the water is heated. A specially constructed receptacle **F** is positioned through the large hole of the stopper **E**, and the receptacle closed with the stopper **G**. The extension **H** is closed with another stopper **I** through which passes a glass spatula **L**.

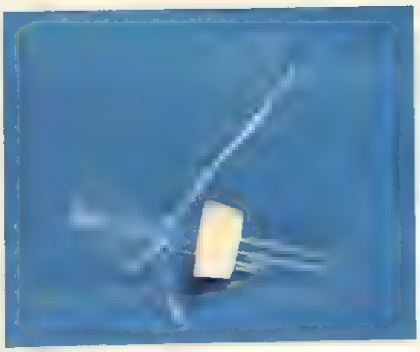
Supported on the spatula is a small glass container **M**, which holds the alcohol. This container is sealed, and quite fragile. When the spatula is withdrawn the container falls to the bottom of the receptacle **F** where it breaks, releasing its contents. This contact with the heat from the surrounding water causes immediate vaporization and a coincident increase in volume. In turn the air-alcohol vapor mixture escapes from the receptacle through tube **N** into the inverted graduate. The graduate is filled with water and immersed in a hydropneumatic bath, as shown; the escaping air-gas mixture displaces an equivalent volume of water from the graduate. Following correction, the volume as measured in the graduate can be used to determine the molecular weight of the ethyl alcohol.

2

a

b

c



**SETTING UP THE [illegible]MENT**—All the equipment can be pu[illegible] from a chemical supply house. The [illegible]ould have at least a 500-ml capacity, [illegible]ld the graduate. Both are firmly suppo[illegible]d the flask must have a wire mesh betwe[illegible]nd the flame to prevent breakage of the [illegible] Illustrations 2a and 2b show the comple[illegible] tup.

Illustration 2c [illegible] receptacle in which the alcohol is vaporiz[illegible] and which is detailed in Illustration 1.

The fragile gla[illegible] container for the liquid alcohol is most [illegible] filled with a syringe, after which the neck of the container is sealed. The latter can be accomplished simply by using a material insoluble in alcohol, such as paraffin.

In setting up the graduated cylinder, care must be taken to assure that it is completely filled with water prior to inversion in the bath; and, most importantly so as to minimize error, the cylinder should not be set over the end of the escape tube (N in Illustration 1) until after the water in the flask has boiled for a minute or so. This allows as much trapped air in the tube to be expelled as possible.

Furthermore, it must be remembered that the gas-air mixture that displaces the water in the graduate is under less than standard atmospheric pressure.

Now, suppose that 436 ml is the amount of gaseous ethyl alcohol (mixed with air and water vapor) observed in the graduate, and that the temperature is 18° C (64.4° F) while atmospheric pressure (from barometric measurement) is noted at 735 mm of mercury. The exact volume of the alcohol, from which its molecular weight is calculated, can be determined by the following operations:

The atmospheric pressure given at the time of the experiment is 735 mm, or 25 mm less than standard pressure. The temperature is 18° C, not 0° C standard temperature. Thus, from the table of partial pressures, this represents 15.477 mm pressure exerted by the water vapor. Therefore, the volume of displaced water in the graduate is calculated:

$$436 \times \frac{735-25}{760} \times \frac{760-15.477}{760} = 399.0217.$$

Now the 18° temperature deviation from standard must be put into the calculation to find exact volume. This is done by multiplying the previous result by $273°/(273+18°)$, or 0.938. Hence, the final value for the volume of ethyl alcohol vapor is 363.365 ml.

# THE DETERMINATION OF SPECIFIC GRAVITY

## analysis of a significant physical property

One very important physical property of matter is its relative specific gravity. For liquids and solids, specific gravity is defined as the ratio of the density of a substance to the density of water at 4° C. The density of a substance is simply its mass per unit volume.

Specific gravity varies widely from one substance to another. For example, osmium, perhaps the most dense of all the elements, has a specific gravity of 22.57, while the specific gravity of liquid hydrogen is only 0.07–14 times lighter than water and 315 times lighter than osmium. Between these two extremes lie the specific gravities of all the other elements.

The great diversity in specific gravity, however, is not of primary interest here. Instead, this article is concerned with the fact that small changes in the purity or the physical characteristics of a substance produce appreciable differences in its specific gravity. As a result, determination of specific gravity constitutes a method of analysis.

The melting point of a substance is determined by degree of purity. It is thus possible indirectly to measure the degree of purity by determining how much a melting point differs from the melting point of the pure substance. The density of a substance is also related to the degree of purity. While density and melting point are indirect measures of a substance's purity, they do not reveal the nature of the impurity, a nature that very often does not matter. In many cases when the identity of the impurity is known, it is more important to determine the degree of impurity. A typical example is measurement of the alcohol content of a wine. The principal ingredient of wine is water. Alcohol—the additive substance—varies the specific gravity of the wine solution by lowering it. The specific gravity of a wine is, therefore, also a measurement of its alcohol content.

Different methods are used to measure specific gravity, depending on whether the substance in question is a solid, a liquid, or a gas. This article describes measurement of the specific gravity of solids and liquids by means of several different techniques. More complex techniques are required to measure the specific gravity of a gas because of the difficulties inherent in the nature of gases.

1

**THE METHOD OF MIXING LIQUIDS**—Determining specific gravity by means of a pycnometer is difficult, if not impossible, when the volume of the object is very small, on the order 1 mm³ or less. In such cases a more efficient method is required. In the method described here, a mixture of two liquids is prepared. These liquids must be miscible in all proportions. Moreover, one must have a low specific gravity and the other a high specific gravity. For the example discussed here, methyl iodide and benzene are used. Methyl iodide has a specific gravity of 3.3, benzene a value of 0.88. This method makes it possible to measure any specific gravity between the two extremes represented by methyl iodide and benzene. Note that this mixture is highly flammable and that suitable precautions must be taken. The procedure is as follows: In a beaker a known quantity of one of the two liquids—the one whose specific gravity is lower—is prepared. For example, if the specific gravity of a fragment of rock is desired, a known quantity of benzene is poured into the beaker. The volume must be precisely measured, perhaps by means of a graduated pipette.

Suppose exactly 10 cm³ of benzene are placed in the beaker along with the unknown object. The object will sink because its density is greater than that of the benzene. As carefully measured quantities of methyl iodide are added and mixed t[hor]ughly with the benzene, however, the spe[cific] gravity of the liquid mixture increases [until] the object of the measurement is to add just [enough] methyl iodide to make the specific gravi[ty of] the liquid mixture exactly equal to the sp[ecific] gravity of the unknown object. This is [done] by observing the rate of fall of the ob[ject] through the liquid mixture after each addi[tion] of methyl iodide. As the mixture's specif[ic] gravity approaches the specific gravity of the object, the rate of fall will decrease. Finally, the rate of sinking will be extremely slow, and the addition of a minute quantity of methyl iodide will cause the object to rise quite slowly. At this point the specific gravity of the liquid mixture equals the specific gravity of the object. A simple calculation now gives this specific gravity value. The total weight of the liquid mixture is equal to the weight of the lighter liquid plus that of the heavier one. The first is 10 cm³ × 0.88 g/cm³ = 8.8 g; the second is 3 cm³ × 3.3 g/cm³ = 9.9 g (assuming the quantity of methyl iodide added was 3 cm³). The total weight of the liquid mixture is, therefore, 8.8 + 9.9 = 18.7g. The volume of the mixture is the sum of 10 cm³ of benzene and 3 cm³ of methyl iodide = 13 cm³. The specific gravity of the solution is, therefore, 18.7/13 = 1.44. This value is the same as the specific gravity of the unknown object.

c

**PYCNOMETER** — The pycnometer bottle provides a relatively simple method for measuring specific gravity. This instrument is simply a glass bottle with a long neck that can be fitted tightly into a ground glass insert. A horizontal mark on the neck indicates the level to which the bottle must be filled with distilled water at a standard, specified temperature to measure standard density. A precision balance is required. To measure the specific gravity of a solid, the following weights are obtained:

1. The first is the weight (designated as $P_1$) of the pycnometer filled with distilled water to the mark on the neck (Illustration 1a).
2. For the second weighing, the object whose density is to be measured is added to the same plate of the scale holding the pycnometer (Illustration 1b). This weight is designated as $P_2$.
3. For the third weighing, the unknown object has been placed inside the pycnometer, thus displacing some water (Illustration 1c). When the neck of the pycnometer is replaced after adding the object, the bottle is filled just up to the mark. This is the equivalent of having dropped the object through the neck of the bottle, and then pouring off the water above the level of the mark. This weight is $P_3$; it will be slightly less than weight $P_2$. These three weighings constitute all of the data needed to determine the specific gravity of the unknown. In this case, since the density of water is 1, the numerical value of the specific gravity of the unknown object is equal to the weight of the object divided by its volume. The weight of the object is obtained by subtracting $P_1$ from weight $P_2$. The volume of the object in cubic centimeters is numerically equal to the weight in grams of the water displaced: $d_{H_2O} = 1$ gm/cm$^3$. This value is thus $P_2 - P_3$. The specific gravity of the object is, therefore:

$$\frac{P_2 - P_1}{P_2 - P_3}.$$

Several factors influence the precision of this determination. One, the volume of the pycnometer must not be too large compared to the volume of the unknown object. A precise measurement of specific gravity is not possible if the volume of the unknown is quite small compared to the volume of the pycnometer. Two, the unknown object must not be soluble in water. If it is, it will decrease in volume and the calculated specific gravity will be incorrect. (To avoid this problem, the pycnometer can be filled with a liquid other than water in which the unknown is insoluble. Another way is to waterproof the unknown by means of a protective coating. This, however, greatly decreases the precision of the method.) Three, the object must not be porous. If it is, its surface must be waterproofed by means of a thin coat of paint, or it should be soaked in the liquid used in the pycnometer prior to the actual measurements of volume but after the measurements of its weight. In the first case, the specific gravity will be low because the volume of the object includes air within the pores. In the second case, the result will be more accurate because a more accurate measurement of the object's volume will have been used. The accuracy of a pycnometer also depends on a constant temperature.

2

**MINIMUM VARIATIONS OF SPECIFIC GRAVITY**—The liquid-mixture method is used also to determine the specific gravity of substances having specific gravity values only slightly different from that of some liquid of known specific gravity. This applies to many plastic materials. Using this method, it is possible to determine the specific gravity of polyethylene (which varies slightly depending on the amount of filler it contains) with great accuracy. For this measurement water is mixed with alcohol. Alcohol has a specific gravity of 0.7893 (the alcohol must be pure and free of water; otherwise this, too, must be taken into consideration). Since the density of polyethylene is only slightly less than that of the water, a few drops of alcohol may be added to a known volume of water to reduce the liquid-mixture specific gravity to the equilibrium point; that is, to the point where the polyethylene neither floats nor sinks. The amount of alcohol needed is easily measured because it is small. Thus, any error in its measurement will only slightly affect the specific gravity value of the mixture. The illustration shows a piece of polyethylene at equilibrium in a mixture of water and alcohol. Although this sample may not be in perfect equilibrium, since it can take many tens of seconds to sink or float, for all practical purposes it is in equilibrium. Its specific gravity is equal to that of the mixture. Thus, the data necessary to calculate it are known.

3

# CAPILLARITY | the rise of liquid molecules

Capillary action, or capillarity, is one of the most important mechanical processes in nature. The process allows, for example, ground water to be drawn into plants through their root systems.

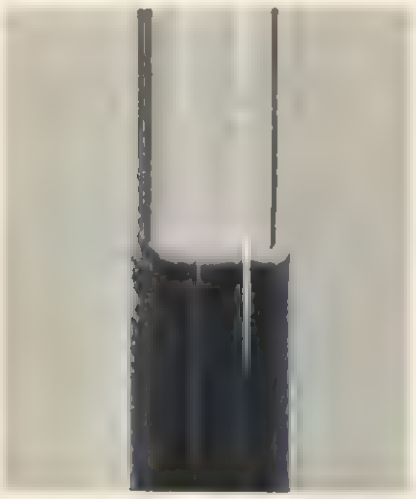
An understanding of capillarity helps explain why, for example, water "climbs" up the threads of the corner of a towel soaked in water. By means of capillarity, a sugar cube is soon soaked almost throughout when only one side of the cube is dipped in coffee. Blotting paper, bandages, sponges, paper towels, and lampwicks perform their expected functions because of capillarity.

Capillary action is produced as a result of the attraction or repulsion of the molecules on a liquid's surface by a solid container of hair-thin dimensions. In a glass of water, for example, the liquid in contact with the sides of the glass appears to rise above the body of water. This is because the surface molecules of the water tend to be attracted toward one another, while at the same time those molecules in contact with the solid glass are attracted to it. Illustration 1 demonstrates this upward creeping. These forces of attraction result in surface tension, or the tendency of liquids to contract at their surfaces. It is almost as though the fluids were manufacturing taut membranes having different physical characteristics from those of the mass.

While a glass of water certainly cannot be called a container having hairlike dimensions, such containers can easily be made. So-called capillary tubes dramatically illustrate the forces at work between a liquid and a solid in contact.

**A CONCAVE MENISCUS**—Surface tension of water in a capillary tube causes the liquid to form a concave layer of molecules, or meniscus.

1



**CAPILLARY TUBES**—Slender and hairlike, these fragile tubes are used to demonstrate interesting and unusual properties of liquids.

2

## JURIN'S LAW

The theory of llary phenomena states that if a tul small internal diameter is dipped liquid (water) capable of wetti rface, the liquid will rise in the tul higher level than that of the fluid hich the tube is immersed. The the diameter of the tube, the gr he height of the liquid column. A ngly, Jurin's law states that this nversely proportional to the radi the capillary. Expressed as an n, Jurin's law is $h=\frac{k}{r}$ where $h$ is th fference between the level reache the liquid in the tube and that of iquid in the container. The radiu the capillary is $r$, and $k$ is a const lependent on the force exerted b molecules of the mass of liquid a se in contact with the capillary wal

To demonstrat is law, capillary tubes can be prep by drawing standard glass labora tubing in a gas burner. Example ubes prepared in this way are sh Illustration 2.

Once the capil have been drawn, each representin fferent diameter, lengths of about m (about 4 in.) should be mount shown in Illustration 3. The vertic d horizontal framing members are and the tubes are held on the horiz piece with water-insoluble adhesive e tubes must extend below the l f the water in the dish. To better lize the results of this experiment, the ater is colored with any soluble dye (food coloring serves quite adequately).

Once the ends of the tubes are immersed, it is immediately seen that the water rises to the highest levels in the capillaries with the smallest diameters. However, to verify Jurin's law, the internal diameter of the capillaries must be measured. One way to do this is by weighing the empty tubes on an analytical balance. This figure subtracted from the weight following immersion will indicate the weight of the water. From this,

the diameter can be calculated on the basis of the capillary's length, or of that portion of it filled with water. For example, if the weight difference is seen to be 3 mg in a tube 5 cm long, the internal diameter of the capillary is about 0.028 mm. Another method uses direct observation. In this case, a small segment of the tube is inserted vertically into some modeling clay on a microscope slide. Under low power, the diameter of the tube is compared to a scale or to some object whose exact dimensions have been determined previously.

## THE EFFECT OF TEMPERATURE

Early experimenters did not take into account the variation of surface tension with temperature. The rise of liquid in a capillary tube was supposed to vary

3

**A QUARTET OF CAPILLARIES**—The colored water shows clearly that the level to which a liquid will rise in a capillary tube is dependent on the tube's diameter.

4

**UNEQUAL RISE OF EQUAL VOLUME**—This connecting vessel demonstrates the power of capillarity. Although the liquid rises higher in the capillary, the volume of water is identical in both legs of the U.

merely because the density of liquids varies. Experiment has shown, however, that surface tension itself—and hence capillarity—in all cases diminishes with rise in temperature. That it will tend to diminish to zero can be inferred from the notion that at the critical state, a liquid and its vapor will become identical; the tension at the interface must then be zero.

## CONNECTING CAPILLARIES

The principle of connecting vessels states, in essence, that a liquid rises equally in all containers having a common base. In preparing this demonstration, one section of the communicating tube must be larger in diameter than that of the capillary. Otherwise, the experiment will seem to contradict the principle.

Illustration 4 shows a connecting vessel constructed from a piece of standard glass tubing. Starting with a tube at least 10 cm long, the U is formed in a Bunsen burner, with one leg of the U longer than the other. The longer section is drawn into a capillary.

When filled with water, the liquid rises to apparently different levels in the two sections of the U, apparently disproving the principle. In fact, the volume of water contained in the sections is identical.

## ANOTHER HYDROSTATIC EXPERIMENT WITH CAPILLARIES

In this demonstration, shown in Illustration 5, two types of capillary are used. One has a wider base than the other, and is nothing more than a piece of the stock from which the fine capillary is drawn. Both pieces should be about 10 cm long.

Before immersion in the dish of water, the larger tube must be filled with liquid, at least above the point at which it narrows into the capillary. When both tubes are dipped into the water in the dish, the liquid rises to the same level in each. This demonstrates that the liquid in the tube having the large base is sustained above the liquid in the dish by capillary attraction in its smaller section.

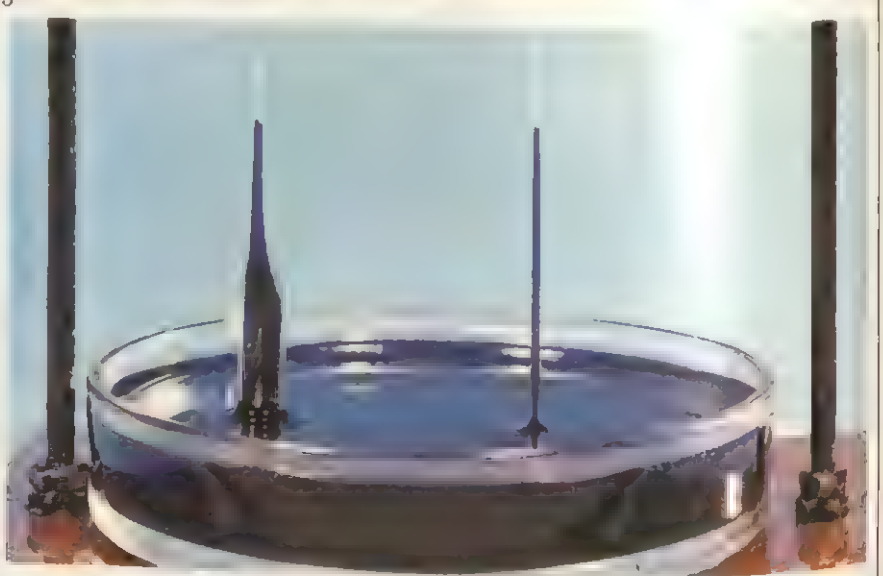
## CAPILLARITY AND THE SOIL

As stated previously ipillarity allows ground water to b wn into plants through their root ns. Plant fibers contain a great ma nute tubes and channels that act in me manner as capillary tubes.

Capillarity in soil natter of great concern in agricult il particles pull water down from t ace or up from an underlying wat e. The smaller the particles of soi the closer together they are, th channels they form between the drawing water. Sometimes after a s the upper layer of soil is packed i rd crust; then, the moisture that on this tightly packed soil evapo nto the air before the soil is abl aw it down to the plant roots.

In regions having t deal of rainfall in early spring y little through the hot summer "dry farming" methods are often ved. First, the soil is plowed dee fine; it is then packed down. Soil les then form channels that draw ture up around the plant roots. The e soil is worked to make a layer of lverized soil. In this layer, as the pa are too loose to form channels, ver water is drawn up to be lost throu poration.

5



**MOLECULAR STRENGTH**—The slender capillary section of the tube on the left supports the proportionately greater volume of water below it through attraction of the liquid's molecules to the capillary walls

# EQUILIBRIA BETWEEN TWO PHASES

## liquid-liquid and liquid-vapor equilibria

A later artic[le] will discuss solid-liquid equilibrium [in] two-component systems. This article [con]tinues the study of two-component s[ystems], but extends consideration to li[quid-]liquid equilibrium and liquid-vapor [equil]ibrium. An important application o[f liq]uid-vapor equilibrium is fractional di[stil]lation, the process used whenever pr[actic]al to separate the pure components f[rom a] liquid mixture of two substances. A[n un]derstanding of liquid-liquid equilib[ria] is thus most useful for extraction or [con]centration of a substance by means of [shak]ing it between two distinct solvent[s].

### LIQUID-LIQUID EQUILIBRIUM

Two liquids [may] be soluble in each other in all proport[ions] (water and methyl alcohol, for ex[ample]) or they may be partially miscil[ible]. A classic example of partially mis[cible] liquids is the system consisting of [water] and ether.

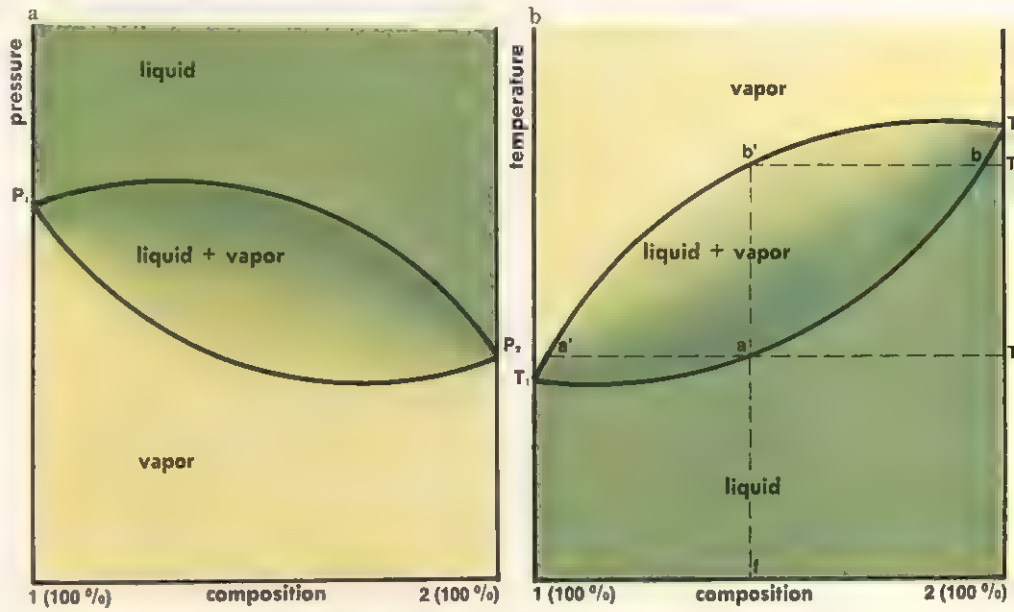
If a small [amount] of ether is added to water in a b[eaker] and stirred, the ether dissolves. As [more] ether is added, however, two la[yers] form. The lower layer has a greate[r den]sity and consists of a saturated sol[ution] of ether in water. The upper layer, [ether], consists of a saturated solutio[n of] water in ether.

Another [well-]known example is the system consi[sting] of water and phenol. As Illustratio[n 2] shows, the solubility of the two subs[tances] in each other increases as th[e] temperature increases. Stratification disappears, however, above 69° C (156.2° F) and the two substances become completely miscible. This temperature is known as the critical solution temperature (B in Illustration 3).

Illustrations 4a, 4b, and 4c show the behavior of a mixture having the composition f (see Illustration 3) at three distinct temperatures; 30° C, 69° C, and 80° C (86° F, 156.2° F, and 176° F).

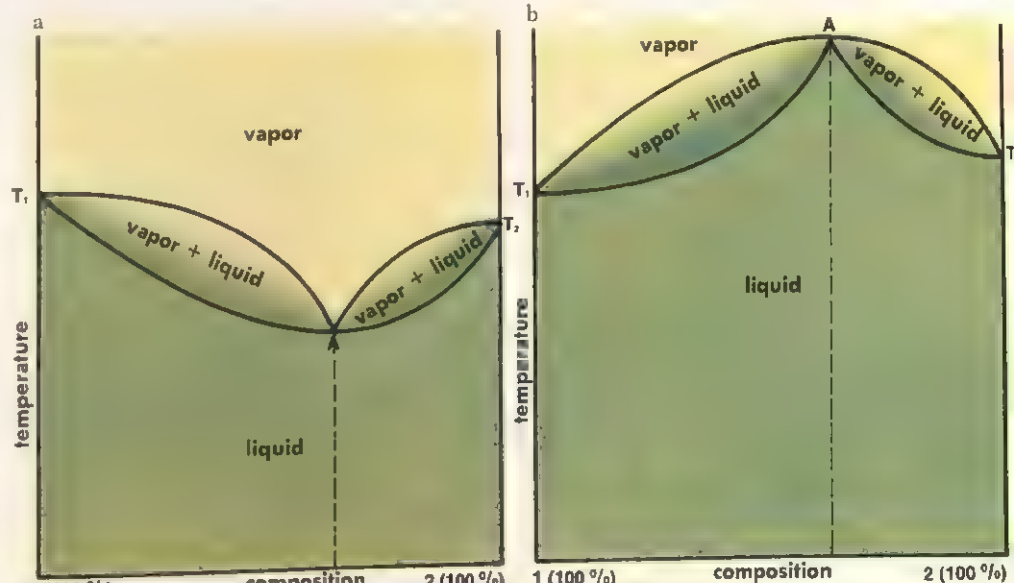
Illustration 4a shows the formation of the two layers. The two solutions in equilibrium are at points e′ and e″ in the graph. The solutions have the concentrations shown along the horizontal axis. The system shown in Illustration 4b is at the critical point B. The clearly visible opalescence is called the critical point opalescence. Finally, in Illustration 4c, the system is at point d in Illustration 3. This is a single liquid phase.

1




**LIQUID-VAPOR EQUILIBRIUM**—In Illustration 1a curves of vapor pressure are plotted against composition (with temperature constant); in Illustration 1b, temperature is plotted against composition (with pressure constant) for a mixture of two liquids. If a mixture having the composition **f** at temperature $T_a$ is considered, the result is a liquid with composition **a** in equilibrium with a vapor having composition **a′**. At temperature $T_b$, on the other hand, a liquid having the composition **b** is in equilibrium with a vapor having the composition **b′**.

2




**EXAMPLES OF AZEOTROPIC MIXTURES**—The azeotropic mixture in Illustration 2a has a vapor pressure greater than that of the pure components. There will, therefore, be a minimum on the boiling curve. In Illustration 2b, on the other hand, the azeotropic mixture has a maximum in the boiling curve (and a minimum in the vapor pressure curve).

If the pressure is constant, the composition of the azeotropic mixture remains constant (point **A** in both graphs).

## LIQUID-VAPOR EQUILIBRIUM

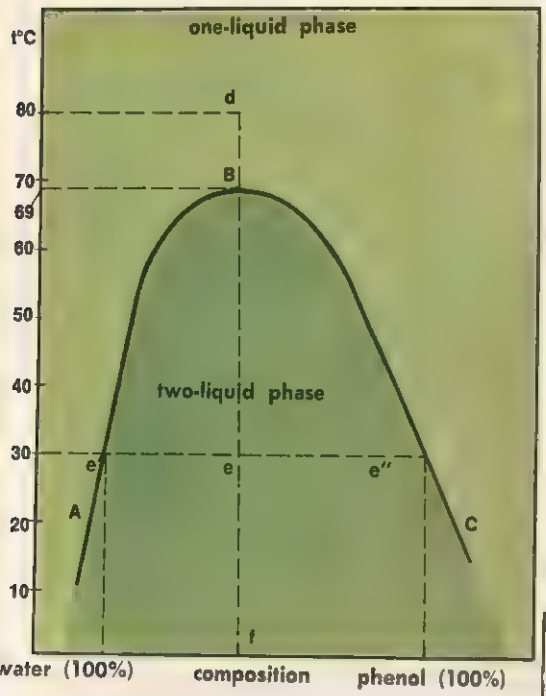
In the most general case, mixtures of two liquids display neither maxima nor minima in the vapor pressure versus composition curves. Two different graphical representations are possible. These are shown side by side in Illustration 1. In the first case (Illustration 1a), temperature is kept constant and the pressure of the system is plotted against composition. In the example shown, substance 1 has a greater vapor pressure than substance 2 at the same temperature. It is, therefore, more volatile. The graph also shows the areas of stability of the liquid and vapor phases.

In the second case (Illustration 1b), which is of greater practical interest, temperature is plotted against the composition of the mixture, with pressure remaining constant. The more volatile substance 1 boils at a lower temperature than substance 2. The vapor curve is above and the liquid curve below.

Consider a mixture having the composition f (Illustration 1b). At temperature $T_a$ the equilibrium system will contain a liquid having composition a and a vapor having the composition shown at point a′. If the temperature is now increased from $T_a$ to $T_b$, the composition of the liquid phase will change from a to b, while the composition of the vapor phase will change from a′ to b′. As the phase diagram shows, no matter what the composition of the liquid phase, the vapor phase in equilibrium with it is always richer in the more volatile component (substance 1). This rule, called Konovaloff's rule, is the basis of fractional distillation.

Fractional distillation is a process that uses successive distillations to separate a liquid mixture of components into the pure state. For example, nitrogen (boiling point −196°C) and pure oxygen (boiling point −183°C) are prepared by the fractional distillation of liquid air. Not all mixtures of liquids, however,

3




**THE WATER-PHENOL PHASE DIAGRAM**—Water and phenol are partially miscible. Once a certain concentration is reached, however, the phenol will no longer dissolve in the water. This is equally true with regard to the solubility of water in phenol. Two liquid layers will thus be formed, one containing an excess of phenol and the other an excess of water. The reciprocal solubility of the two substances becomes greater as the temperature increases. **ABC** is the solubility curve.

There are also cases of systems (such as the one shown in Illustration 5) that have an inverse critical temperature; that is, systems in which the reciprocal solubility of the two liquids diminishes as the temperature increases.

Illustration 6 shows the unusual system consisting of water and nicotine. This system displays a completely closed zone of miscibility. Therefore, the system simultaneously possesses both an upper and a lower critical solution temperature.

The presence of impurities in systems such as these, even in minute quantities, normally causes considerable variation in the location of the critical point. This phenomenon can be exploited, however, for determining the degree of purity of some compounds (hydrocarbons, for example).

4

**BEHAVIOR OF A WATER-PHENOL MIXTURE**—Consider the behavior of a water-phenol mixture with composition f (see Illustration 3). At a temperature of 3( e), the mixture form composition repres presented by point vers that have the ′ e′ and e″ (illus-

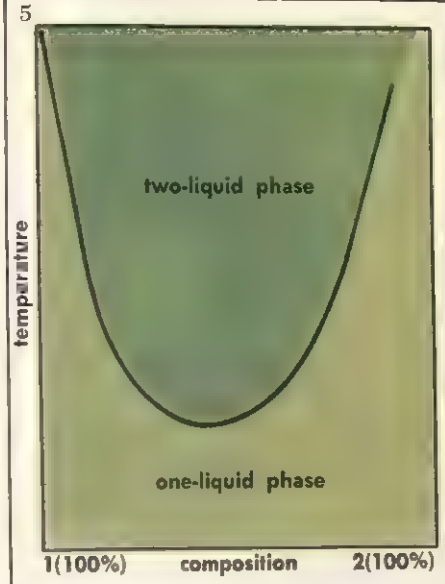
a

behave as in the example shown in Illustration 1.

In many instances liquid-vapor equilibrium mixtures have a vapor pressure that is either greater (Illustration 2a) or smaller (Illustration 2b) than the vapor pressures of the pure components. Such systems are known as azeotropic mixtures —mixtures that boil unchanged.

It is not possible to separate the components of these systems by fractional distillation. In fact, it does not matter if the fractional distillation starts with a mixture containing an excess of component 1 or a mixture containing an excess of component 2. In either case, the distillation product will consist of a pure component and the mixture of the two components. The mixture will have a unique composition known as the azeotropic composition and the system is said to exhibit maximum or minimum azeotropy. If the pressure is constant, the azeotropic composition will always boil at a given temperature.

5




**A SYSTEM WITH A LOWER CRITICAL SOLUTION TEMPERATURE** — As this graph shows, the reciprocal solubility of the two components 1 and 2 diminishes as the temperature increases.

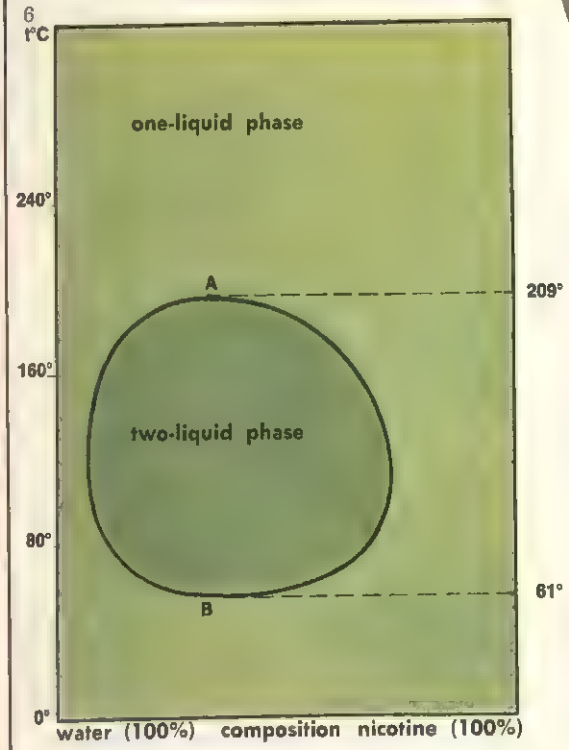
An example of an azeotropic mixture having a boiling point lower than either of the pure components is water (boiling point 100° C) and pyridine (boiling point 116° C). This mixture forms an azeotrope that contains 60 percent pyridine and boils at 91° C.

An example of an azeotropic mixture having a boiling point higher than either of the pure components is acetone (boiling point 56° C) and chloroform (boiling point 61° C). This mixture forms an azeotrope containing 80 percent chloroform; it boils at about 65° C.

In order to understand the curves of Illustration 2, the analogous curves of Illustration 1 should be referred to. The curves of Illustration 2 consist (in a purely formal manner) of the two simpler curves of Illustration 1. Point A identifies the azeotropes.

tration 4a). At a ature of 69° C (represented by point mixture has become opalescent. This critical solution temperature or critical mixing point (Illustration 4b). Finally, at a temperature of 80° C (point d), a clear mixture is produced (Illustration 4c).

6




**THE WATER-NICOTINE SYSTEM**—In this example there is an upper critical solution point A ($T_A$ = 209° C) and a lower critical solution point B ($T_B$ = 61° C).

# SOLUBILITY | solid-solution equilibria

When a substance (the solute) is placed in a liquid (the solvent) capable of dissolving it, a solution forms. The term solution is applied to physically and chemically homogeneous mixtures consisting of two or more components whose composition can vary in a continuous manner within well-defined limits. It is important to note that solute particles must be dissolved to form a solution. If the solid particles are suspended in the liquid, the mixture is called a suspension rather than a solution.

## THE CONCENTRATION OF SOLUTIONS

The term concentration defines the quantity of solute present in a given quantity of solution. Concentration can be expressed in various ways:

1. Grams of solute per 100 g of solution (percent by weight).
2. Weight of solute per unit volume of solution.
3. Volume of solute per 100 volumes of solution (valid only in the case of solutions consisting of liquids, percent by volume)
4. Weight of solute per unit weight of solvent.

In more specific chemical terms, concentration can also be expressed as:

1. The number of moles of solute per liter of solution (molarity).
2. The number of moles of solute added to a liter of solvent (molality).
3. The number of equivalents per liter of solution (normality).
4. The ratio of the number of moles of a component to the total number of moles of components of the solution (mole fraction).

Experience teaches that the addition of solute to solvent cannot continue indefinitely. At a certain point the solute will no longer dissolve; this point the solution is said to be saturated. The solute concentration in a saturated solution at a given temperature is the solubility of the substance at that temperature. Saturation exists when the solution of a substance is in equilibrium with undissolved solute. The number of molecules that dissolves per unit time is equal to the number of molecules that come out of solution per unit time. Thus, the equilibrium in a saturated solution with excess solute is a dynamic rather than a static solution. Some of the solute is constantly going into solution while an equal amount is crystallizing.

## THE LAW OF MASS ACTION

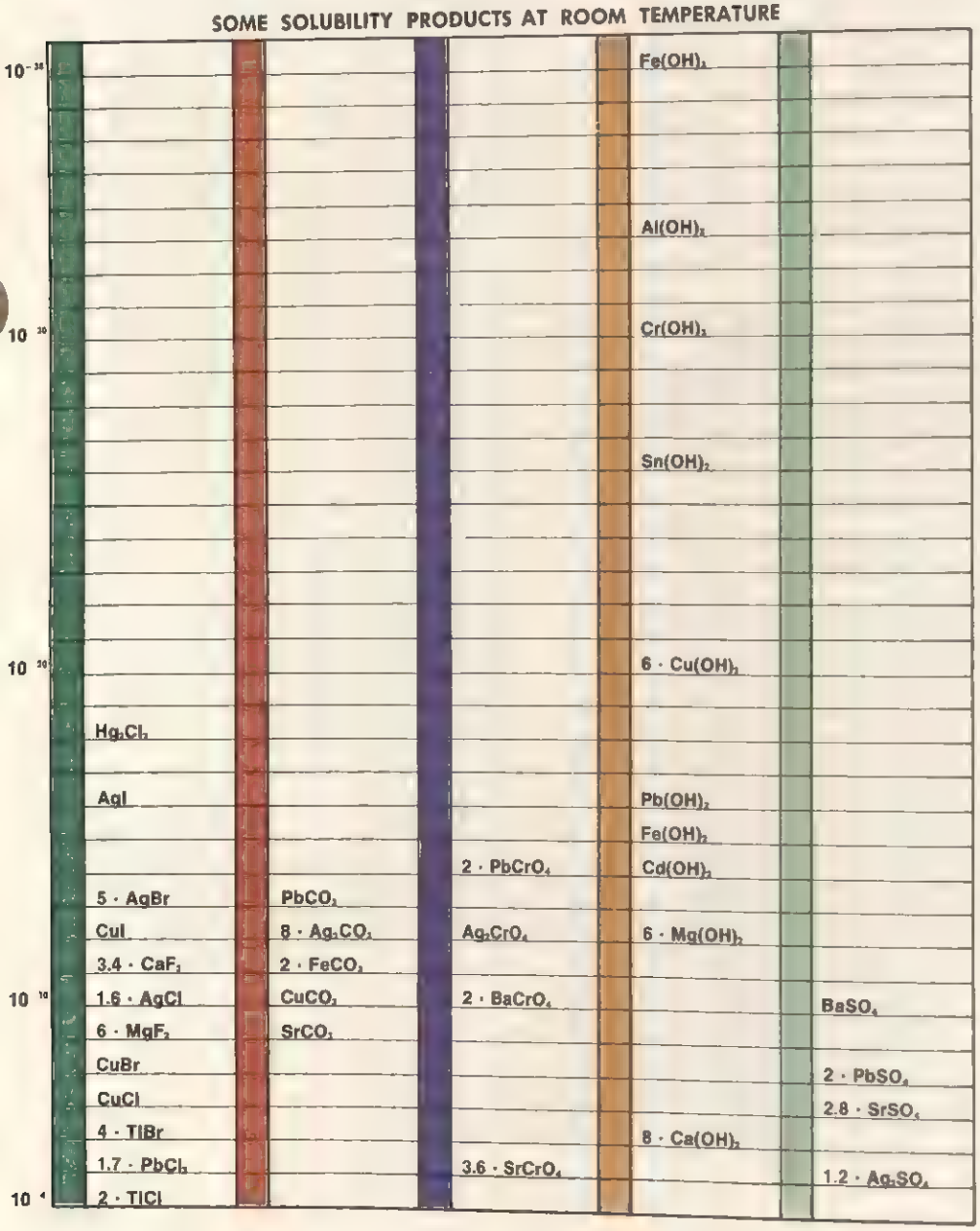
A reaction is reversible when it can proceed either in one direction (with formation of products) or in the other (with formation of the original reagents). The actual direction of a reaction depends on the conditions under which the process is taking place. Equilibrium occurs when the speed of reaction is the same in both directions. For example,

$$A + B \underset{V_2}{\overset{V_1}{\rightleftharpoons}} C + D$$

where $V_1$ and $V_2$ are the forward and reverse reaction speeds.

The speed of a reaction at constant temperature is directly proportional to the concentrations of the reacting species.

SOME SOLUBILITY PRODUCTS AT ROOM TEMPERATURE



This is expressed as follows:

$$= k_1 [A] [B]$$
$$= k_2 [C] [D],$$

where [A], [B], [C], and [D] are the concentrations of the reacting species.

Under equilibrium conditions $V_1 = V_2$, therefore,

$$k_1 [A] [B] = k_2 [C] [D].$$

Dividing both sides by $k_2$ and also by [A] [B] we get

$$k_1/k_2 = [C] [D] / [A] [B].$$

However, the ratio of two constants is also a constant, the expression can be simplified

$$K = [C] [D] / [A] [B].$$

This is known as the law of mass action. It is also known as Guldberg and Waage's law. K is called the equilibrium constant for this reaction.

## SOLUBILITY PRODUCT

Considering a solution of salt XY in the presence of undissolved salt, the following relation holds:

$$XY \rightleftharpoons X^+ + Y^-.$$
(solution)

The law of mass action might be applied to this case. It has been found not to be completely valid, however, for strong electrolytes. Although strong electrolytes should be completely dissociated in solution, this is not the case because the oppositely charged ions attract each other. This must be taken into account if the law of mass action is applied. Thus, a correction coefficient—the so-called activity coefficient—becomes necessary. The concentration of the electrolyte as if it were completely dissociated must be multiplied by this coefficient.

In the case of a strong electrolyte that is only slightly soluble, the saturated solution will contain comparatively few ions. In this case, the law of mass action can be applied.

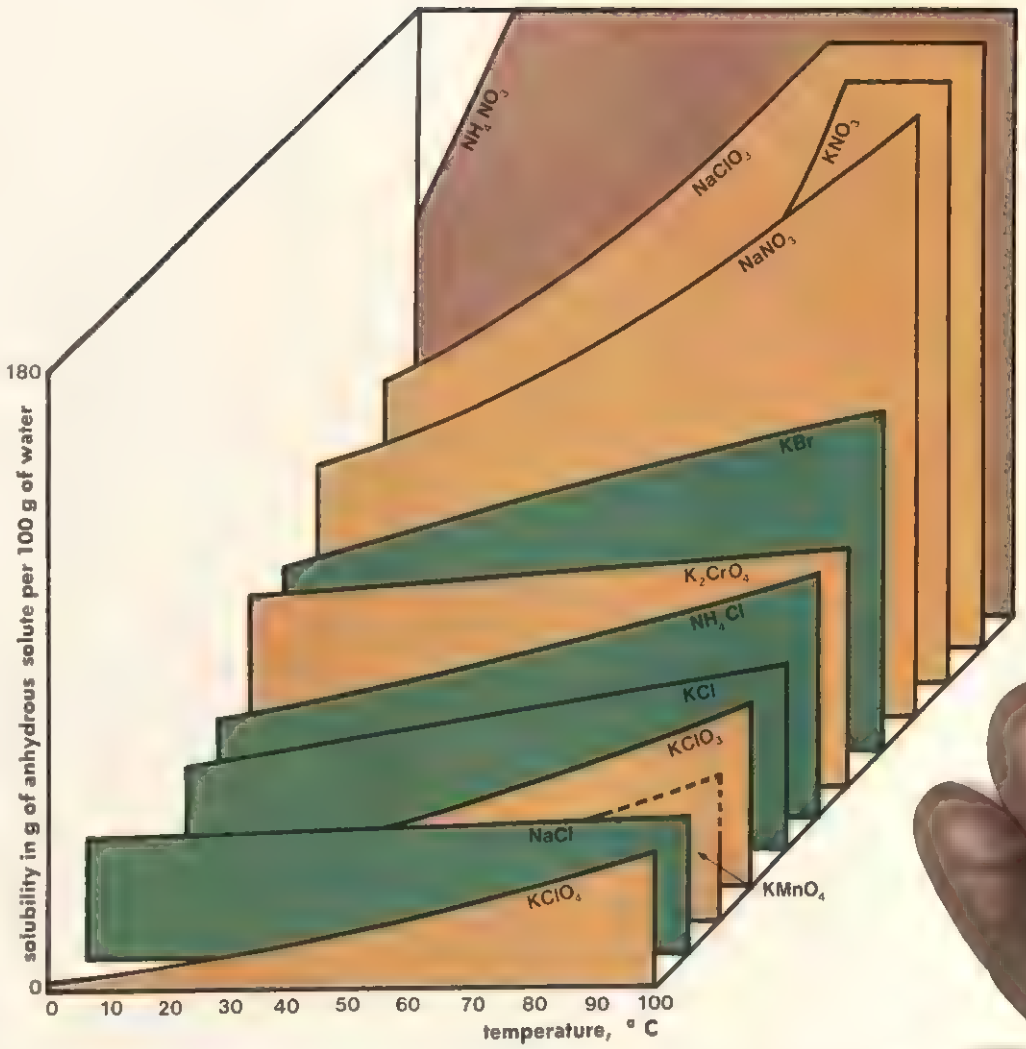
$$k = \frac{[X^+] [Y^-]}{[XY]}$$

Because some undissolved salt is in equilibrium with the solution, the value of the denominator of the fraction is constant. Moreover, the small quantity of salt that dissolves can be considered completely dissociated because the salt is a strong electrolyte. The following expression can therefore be written

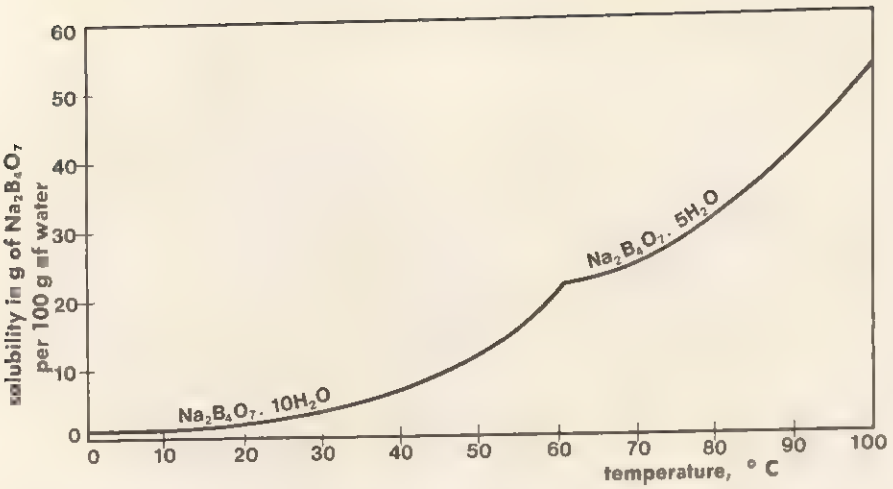
$$K_{xy} = K [XY] = [X^+] [Y^-]$$

The new constant $K_{xy}$ is called the solubility product of the salt XY. Its value remains constant for a given solute and a given solvent at constant temperature. It is not, however, necessary to have undissolved salt in order to have a saturated solution. Rather, it is sufficient for the solution to be unable to dissolve additional solute. In practice, saturated solutions are prepared as follows: A predetermined volume of solvent is treated with an excess of solute, and allowed to stand until the system has reached equilibrium. Excess solute is then filtered out.

Precipitation occurs when the product of the concentrations of the two ions in solution is greater than the value of the solubility product of the salt. At this point the dissolved salt will precipitate; this precipitation will continue until the product of the concentrations of the two ions in solution is equal to the value of




**SOLUBILITY CURVES OF SOME SALTS IN WATER** — This graph shows the solubility curves of several different salts in water. The temperatures are plotted along the x axis; the y axis shows the solubility in grams of anhydrous solute per 100 g of water. At a given temperature, the concentration of solute in a saturated solution is called the solubility of the substance at that particular temperature. As the graph indicates, many of the salts are more soluble in hot water than in cold water. The solubility of others, however, increases only slightly as the temperature rises. In addition, there are some rare cases where the solubility decreases as the temperature of the solvent increases.




**THE SOLUBILITY OF BORAX**—Between 0° and 60° C (32° and 140° F) a saturated aqueous solution of borax ($Na_2B_4O_7$) is in equilibrium with the decahydrate solid phase ($Na_2B_4O_7 \cdot 10H_2O$). Above 60° C, however, it is in equilibrium with the pentahydrate solid phase ($Na_2B_4O_7 \cdot 5H_2O$). The solubility of borax in water is always expressed as grams of anhydrous borax per 100 g of water, regardless of the stable solid phase at the temperature of the solution. The *y* axis shows the concentration in grams of $Na_2B_4O_7$ per 100 g of water. As the the graph indicates, the solubility of decahydrate borax increases with temperature. The solubility of pentahydrate borax increases even more markedly with an increase in temperature.

the solubility product. On the other hand, if a saturated solution is in the presence of a precipitate, the precipitate will dissolve if to the solution a reagent is added that lowers the concentration of one of the ions in solution. It is extremely important to know exactly how many grams of a given substance will dissolve in a certain volume of solvent.

Solubility depends on the nature of the solvent and solute, the temperature, the pressure, and the interactions that take place between solute and solvent. Such interactions are the attractive forces between molecules of solute, between molecules of solvent, and between solvent and solute molecules.

With regard to the nature of solute and solvent, the greater the similarity between their electrical properties, the greater the solubility. In other words, a solute that is easily ionized or dissociated will be extremely soluble in solvents having a high dielectric constant (strongly polar substances), while a solute that is not strongly ionic will tend to be soluble in nonpolar solvents.

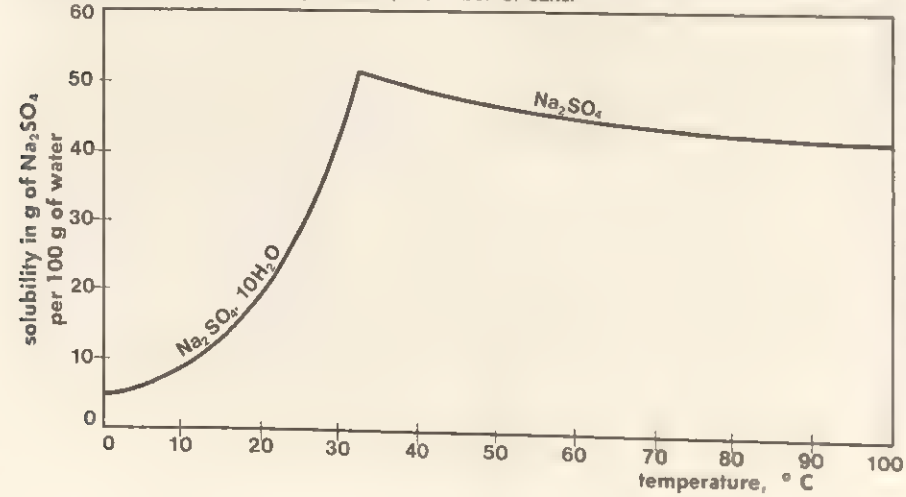
Inorganic salts, for example, dissolve readily in water and in polar solvents such as liquid ammonia, while organic substances are soluble in low-polarity solvents such as acetone, alcohol, carbon tetrachloride, and chloroform. With regard to temperature, Le Châtelier's principle applies. This principle, first enunciated in 1888 by the French chemist Henri Louis Le Châtelier, states that if a chemical system at equilibrium is subjected to a change, processes occur that tend to counteract that change. If the pressure of a system is increased, for example, the equilibrium displaces in the direction that leads to a decrease in pressure.) The solubility of a solid solute is only slightly influenced by pressure because little change takes place in the volume of the system during the process of solution. Solubility is strongly influenced by temperature, however. When the solution of a salt is accompanied by the absorption of heat, an increase in temperature increases the solubility of the salt. The reverse is also true. On the other hand, when the solution process is accompanied neither by the absorption or emission of heat, temperature variation has no effect on solubility.

Generally, however, solution process is endothermic; an increase in temperature brings about an increase in solubility. In some instances the effect of temperature is considerable. In the case of potassium nitrate, for example, 12 g of the salt dissolve in 100 g of water at 0° C (32° F), but this figure increases to 138 grams at 70° C (158° F). In other cases the effect is very small. Indeed, the solubility of sodium chloride in water, for example, is practically unaffected by an increase in temperature.

In the case of salts that are quite soluble in hot water (potassium nitrate and sodium nitrate, for example), it is sometimes possible to prepare two saturated solutions with different boiling points. The first, for example, is a solution of water saturated with potassium nitrate; the boiling point of this solution is 119° C (246.2° F). The second is a solution of liquid (molten) potassium nitrate saturated with water—its boiling point is 310° C (590° F). Furthermore, the difference in solubility of a solute in hot and cold solvents is often used in the laboratory for the purpose of purification by crystallization. For example, the product of many organic reactions consists of a mixture of substances (reactants, products, and products of side reactions) in which the desired product predominates. In such cases, a solvent is selected in

**THE SOLUBILITY OF SODIUM SULFATE**—The solid phase of $Na_2SO_4 \cdot 10H_2O$ is stable up to 32° C (89.6° F). Its solubility in water (expressed in g of $Na_2SO_4$ per 100 g of water) increases very markedly with temperature, as the graph shows. Above 32° C, however, the stable phase is anhydrous. The solubility of this phase decreases as temperature increases.

A decrease in solubility as temperature increases is found only in a very limited number of salts.



which the desired product is extremely soluble at high temperatures. The hot, saturated solution is then prepared and allowed to cool. During cooling much of the desired product will precipitate, while most of the impurities will remain in solution. A great many substances can be purified by successive treatments of this type. The method is practical and presents no difficulty other than the choice of an appropriate solvent.

## THE COMMON ION EFFECT

If a salt that has an ion in common with the solvent is added to a solution, the solubility of the solute diminishes. For example, the solubility of silver chloride, AgCl, in a solution of sodium chloride, NaCl, is less than it is in pure water. The chloride ($Cl^-$) ion is the common ion. If sodium chloride is added to a solution of hydrochloric acid, a precipitate of silver chloride is produced because the equilibrium

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

is superimposed on the equilibrium

$$AgCl \rightleftharpoons Ag^+ + Cl^-,$$

which has the following solubility product:

$$K_{AgCl} = [Ag^+]\,[Cl^-].$$

The addition of the $Cl^-$ ion to the solution thus increases the product $[Ag^+]\,[Cl^-]$ to the value $K_{AgCl}$. Since this value cannot be exceeded, AgCl will precipitate. This phenomenon is known as the common ion effect.

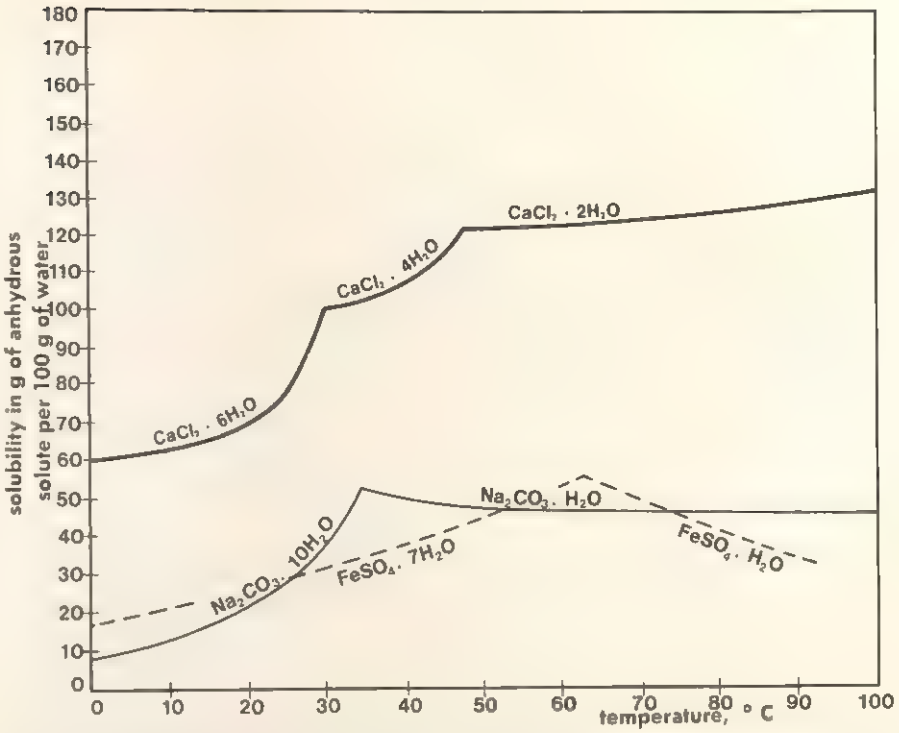
Extraneous ions also have an effect on solubility. This effect, however, is quantitatively smaller and qualitatively opposite to the common ion effect. In fact, the presence of extraneous ions in a solution increases the solubility of certain substances.

This is due to the fact that the correct expression for the solubility product is

$$K_{XY} = [X^+]\,[Y^-] \cdot f_x \cdot f_y,$$

where $f_x$ and $f_y$ represent the activity coefficients of $X^+$ and $Y^-$. Solving for $[X^+]\,[Y^-]$,

$$[X^+]\,[Y^-] = \frac{K_{XY}}{f_x \cdot f_y}.$$




**SOLUBILITY CURVES OF SALTS**—This graph shows three examples of solubility curves of hydrated salts. The solubilities of $CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 4H_2O$, and $CaCl_2 \cdot 2H_2O$ all increase within their respective ranges of stability. The solubility of $Na_2CO_3 \cdot 10H_2O$ also increases, but the solubility of $Na_2CO_3 \cdot H_2O$ remains almost constant as the temperature rises still further. Finally, the solubility of $FeSO_4 \cdot 7H_2O$ increases with temperature, but $FeSO_4 \cdot H_2O$ shows a marked decrease in solubility as temperature increases.

It is known, however, that $f_x$ and $f_y$ can only assume values between 0 and +1, and that these values depend on the quantity of ions present in the solution. Thus, since $K_{XY}$ is a constant, a decrease in the value of the activity coefficients (when the concentration of ions increases, and an increase occurs in the attraction between ions) must increase the solubility of XY.

The effect of extraneous electrolyte increases proportionately with the valence of its ions. This effect also increases as the concentration of the electrolyte itself becomes greater.

Considering the so-called law of distribution, if a certain quantity of a substance is added to a system of two immiscible liquids, and the substance is soluble in both the liquids, the substance will then divide between the two solvents.

This division will occur in such a way that the ratio between the concentrations in the two phases remains constant and equal to the ratio of the solubilities of the substance in the two solvents. In other words, if $c_a$ and $c_b$ are the concentrations of the solute in solvents A and B, then

$$c_a / c_b = K.$$

This is the principle underlying extraction with solvents, a process widely used in organic chemistry both for extracting substances from solutions or from solid mixtures and for purifying the substance.

Although the term solution usually suggests a liquid solvent, it applies equally to mixtures of gases. Air is basically a solution of gases.

There are also solid solutions. For example, ordinary alum $KAl(SO_4)_2 \cdot 12H_2O$ and chrome alum $KCr(SO_4)_2 \cdot 12H_2O$ have crystals so nearly alike in form that they crystallize together from a water solution.

Many life processes depend on solutions. Oxygen from the lungs goes into solution in blood plasma, and the products of digestion are carried in solution to the different parts of the body. The dependence of life on the freedom of complex molecules in solution to move and rearrange is strikingly shown by the cessation of life processes in freezing.

# DIFFUSION IN SOLIDS | the motions of atoms a[illegible] the Kirkendall effect

Consider the crystal lattice of a solid. Ordinarily this brings to mind a stable and nondeformable structure whose atoms are locked in place and cannot move without disrupting the structure itself. This view is incorrect. At best, it can only be regarded as a first approximation. In reality, the atoms of a solid can change their positions. Phenomena associated with this atomic movement within a solid structure are known as diffusion phenomena.

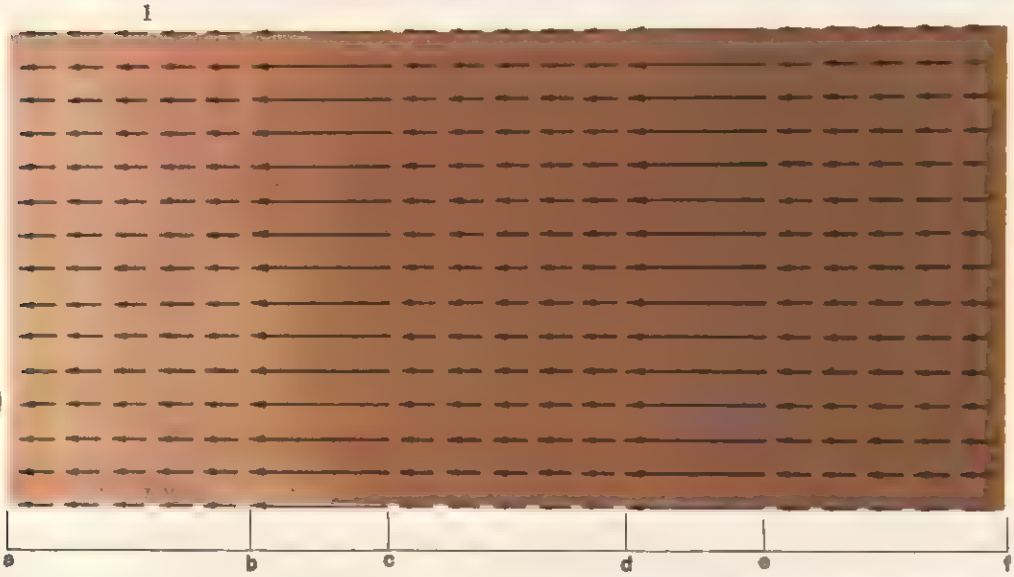
Knowledge of atomic [illegible]ucture is helpful in understanding th[illegible] important diffusion phenomena. Dif[illegible]n is the principal process by whic[illegible]tallic alloys are formed. It also gov[illegible] many of the transformations that t[illegible]place within

**DIFFUSION IN A FLUID**—Consider the volume of a fluid containing some other substance shown here. The fluid may be regarded as a solvent that fills the entire space. Another substance, the solute, has been added to the solvent (the solute is shown in the illustration by the more intense color[illegible] No mixing has taken place; thus the fluid[illegible] perfectly at rest. As a result, there is a diff[illegible] in the density of the solute between one[illegible] of the solvent space and another. There[illegible] vements of the molecules, however, will le[illegible] he solute molecules to move about within[illegible] solvent. In this case the diffusion will t[illegible] place without further heating.

The mathematical law [illegible]licable to this case is a very simple one[illegible] $= -D(\Delta C)$. $J$ is the flow of diffusing mole[illegible]s; that is, the number of molecules that p[illegible] through an area of 1 cm$^2$ perpendicular to t[illegible] direction of motion during the course of th[illegible] ffusion. $C$ is the concentration of the solute[illegible] $\Delta C$ is a vector whose length is proporti[illegible] to the rate of variation of the concentrati[illegible] d whose direction is toward the maxim[illegible] te of variation of the concentration. $D$, o[illegible] other hand, is a constant that depends o[illegible] medium within which the diffusion occur[illegible] on the nature of the solute undergoing [illegible] on. $D$ is called the diffusion coefficient

In this idealized expe[illegible] the solute is concentrated in three zon[illegible] the right zone of the concentration is h[illegible] almost homogeneous. In the middle z[illegible] d the concentration is somewhat lower [illegible] ce again fairly

1

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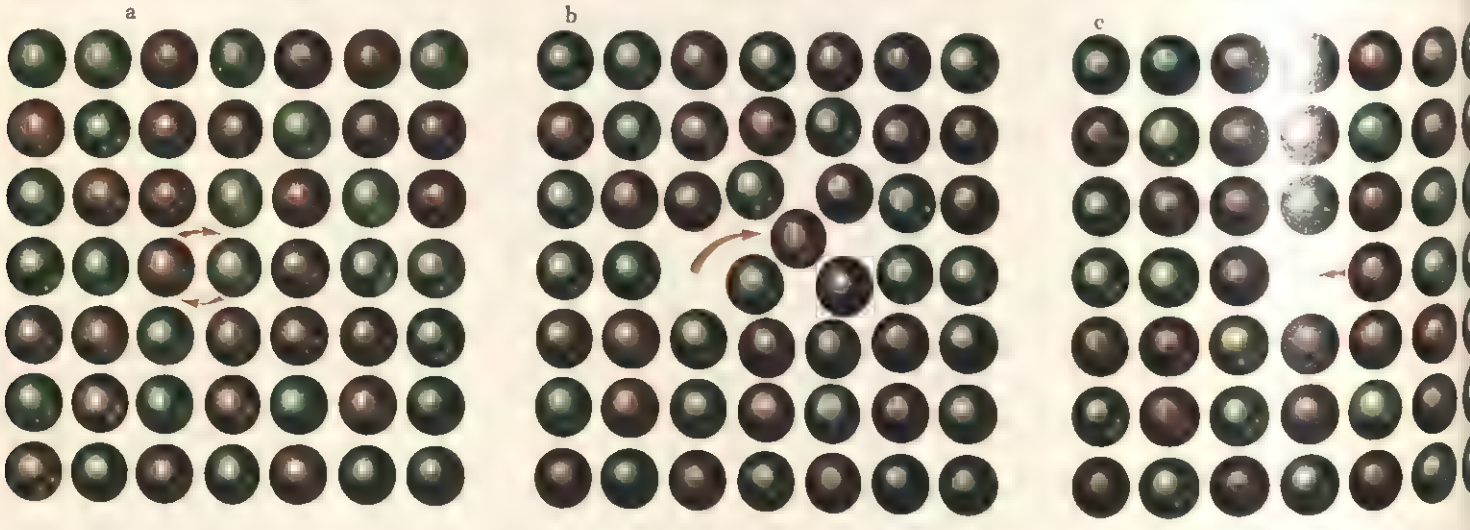



**ELEMENTARY PROCESSES OF DIFFUSION**—These three illustrations show the basic processes of diffusion in the solid state. The first process is direct exchange (illustration 2a). Two neighboring atoms switch positions. The illustration shows a pair of dif-

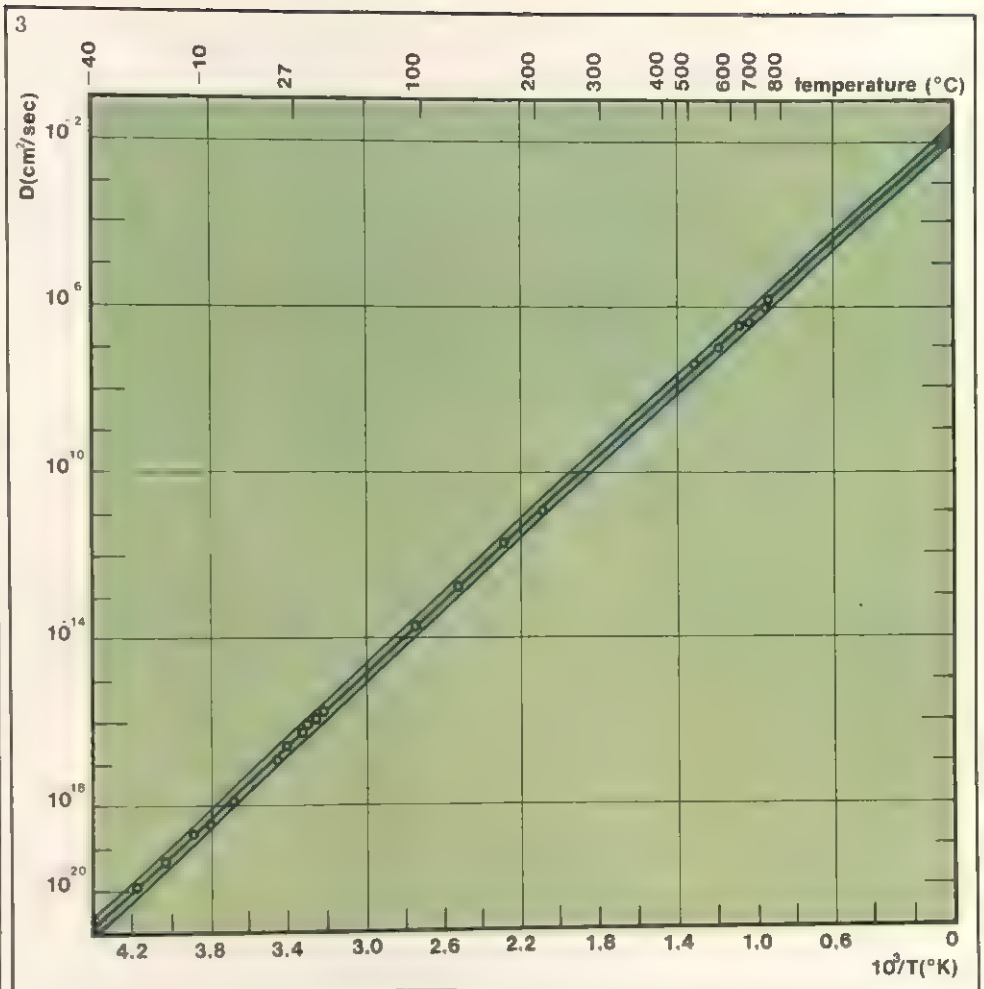
these alloys, and is responsible for their aging. Diffusion is the process that underlies a special type of welding between metals. Moreover, it governs other phenomena in solids, including conductivity in the half... of the alkali metals.

Chemical rea... in which a solid phase plays a p... e also affected by diffusion pheno... For example, diffusion phenome... ocks are extremely important. In fact, cases occur where very rapid diffusion is possible in rocks because of heat. In other cases, diffusion takes place extremely slowly. In such cases the very long duration of geological history permits diffusion phenomena to occur.

homogeneous. In t... one **ab**, however, the concentration is e... er, although still homogeneous. Conse... the gradient in each of these zones is... These gradients are represented by the... vectors directed from right to left. Ther... rger gradient, on the other hand, at th... aries between zones **bc** and **de** beca... density variation is great in these reg...

Under these c... the speed of diffusion of the solu... rvals **ef, cd,** and **ab** will be low. The di... peed will be greater, however, over the... s **de** and **bc.**

Nevertheless, th... s just a first approximation; it is appli... only to liquids. In the case of liquids th... cules are essentially free to move abo... y do not occupy the relatively fixed p... of solid molecules. Note also that liqu... sion, which proceeds spontaneously, oc... accordance with the laws of thermodyn... In fact, solute molecules concentrate... e portion of the solvent space will di... ontaneously until the solute density th... t becomes constant. This increases the... y of the system and diminishes its fre... The process of diffusion in solids als... for the free energy to be diminished.




**TEMPERATURE AND DIFFUSION**—Statistical mechanics enables calculation of the diffusion coefficient, which is a function of the temperature. This coefficient $D$ is small at low temperatures and large at high temperatures.

The values of $D$ are given by the expression $D = D_o\, e^{-H/kT}$, where $D$ is the cofficient at a given temperature $T$, where $D_o$ is the same coefficient at a reference temperature, $e$ is the base of natural logarithms, $H$ is an activation constant of the displacement reaction of the atoms, $k$ is Boltzmann's constant, and $T$ is the absolute temperature.

If this relationship is valid, then the experimentally measured rates of diffusion at different temperatures will produce a straight line when plotted on a semilogarithmic scale.

This diagram verifies the relationship for the diffusion of carbon in alpha iron. This type of diffusion occurs in the formation of alloys of iron and carbon.

ferent atoms. This ... of diffusion, however, can occur between ... cal or almost identical atoms—for examp... tween two isotopes of the same element...

A second basic ... ion process is migration across interst... positions (illustration 2b). A vacancy is cr... d when an atom moves into the interstitia... e from a lattice position. The migrating ... can then go from this interstitial position ... another interstitial position.

Another basic diffusion process depends on the existence of vacancies (illustration 2c). An atom located in a position next to a vacancy can move over and fill the vacancy. This, however, creates another vacancy. If another atom then fills this second vacancy, there is a flow of matter in one direction and a flow of vacancies in the opposite direction.

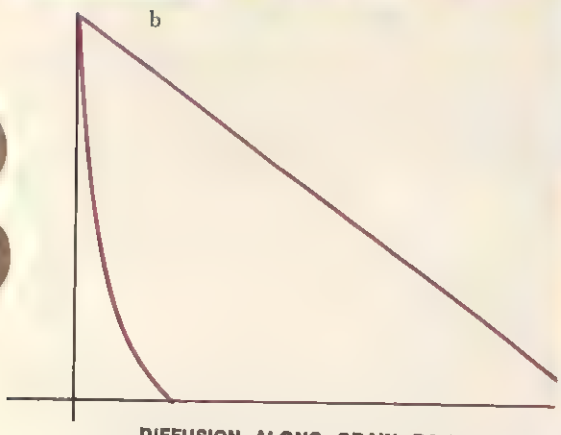
Fundamental rules control diffusion. The first is that in all three cases the diffusing atom must overcome a potential barrier. Consider again, for example, the process shown in illustration 1a the two atoms are stable in both the first and second positions. If these two atoms move from one position to the other, however, the surrounding atoms must be displaced. This requires a certain energy input, and constitutes a potential barrier that must be overcome. The same condition applies to the other two cases. Thus, diffusion requires a certain amount of activation energy before it can take place.

A further observation is suggested by illustrations 2b and 2c. The presence of such crystal defects as interstices and vacancies makes the diffusion mechanisms shown possible. This is further confirmation that crystal defects make possible certain phenomena characteristic of solids. These observations prompt the hypothesis that an increase in temperature produces an increase in these types of defects and thus helps the atoms overcome the potential barrier. Diffusion, therefore, proceeds more rapidly at higher temperatures. Finally, note that the movement of an atom with respect to its neighbors constitutes a type of chemical reaction. An atom originally bonded to one group of atoms will be bonded to different atoms after any one of the three diffusion movements illustrated.

4

a

b

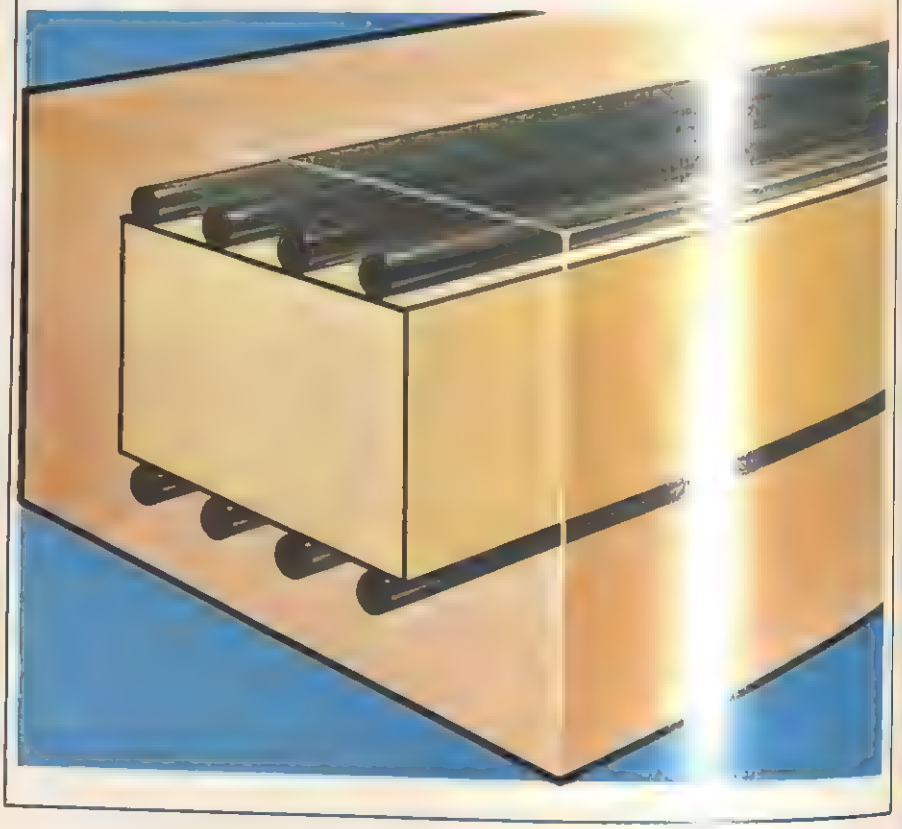


**DIFFUSION ALONG GRAIN BOUNDARIES**—Diffusion in a polycrystalline substance occurs within the grains of the individual crystals. It occurs with greater speed, however, along the grain boundaries, because of structural defects at the boundaries. These defects are the result of sudden changes in the orientation of the crystal lattices and the presence of impurities that favor the formation of defects. Therefore, if a crystal is placed in contact with a different substance that can diffuse into the crystal (illustration 4a), and the concentration of this substance at the various points of the crystal is measured after a period of time, it will be noted that the density of the diffused substance diminishes exponentially at two rates (illustration 4b). This situation is unstable, however, because the diffused substance will eventually diffuse from the boundaries into the crystals themselves. Diffusion along the grain boundaries increases the overall rate of diffusion.

**THE KIRKENDALL EFFECT**—Shown is a core of alpha brass surrounded by pure copper. Molybdenum wires are inserted between the two layers of metal to mark the boundary between the copper and the brass. If not marked, this boundary could easily become lost during diffusion. Now, if the diffusion is activated by heating, the molybdenum wires displace toward the interior of the body. This phenomenon, known as the Kirkendall effect, provides an explanation of the mechanism governing diffusion between copper and brass. If the diffusion occurred by means of a simple exchange during which a copper atom replaces a zinc atom, no transport of matter would take place. Zinc is far more prone, however, to exchange places with a vacancy than to exchange places with a c per atom. The zinc atoms will, therefore, lea e brass area quite readily. The copper at however, do not penetrate the brass so ly. The alloy will, therefore, become riche vacancies; it will not become diluted wit per, as might be expected. These vacan will then cause an increase in the volum ne system. In any case, the flow of vaca to the brass alloy is sufficient to lower it sity and create a porosity that is readily red.

Diffusion experiment e type described are of fundamental im e in determining the mechanisms gove iffusion phenomena.

5



The study of diffusion begins with a mathematical theory of the phenomenon. This theory describes diffusion as follows, in agreement with experimental evidence: two different substances in contact will diffuse into each other at a rate proportional to the concentration difference between the two substances and in the direction the concentration difference varies most rapidly. This definition is rigorously valid, however, only in the case of homogeneous fluids. For example, if lampblack is made to diffuse into a fluid gelatin, the lampblack will be distributed throughout the gelatin according to an exponential law that is so accurate that a section cut from the block of gelatin can be used to construct an optical wedge, that is, a densitometric wedge. Even though the lampblack is not a fluid, the law will hold if the dispersing medium is a fluid. In this instance it is not necessary to take into account any special forces between the lampblack and the liquid.

Diffusion in solids must be considered a type of chemical reaction. Thus, it is not sufficient to describe diffusion solely on the basis of concentration. It must also be thermodynamically possible. Then it is possible to deal with the problem of diffusion in solids.

The phenomen[illegible] adsorption concerns the interaction [illegible]een the surface of a liquid or a sol[illegible]known as adsorbents) and particular [illegible]ances (known as adsorbates). Th[illegible]raction in question must occur o[illegible] the surface and is connected wi[illegible]rticular forces discussed in this [illegible] On the other hand, a uniform per[illegible]on into the whole of the body of t[illegible]d is a simple case of mechanical ab[illegible]on that must not be confused wit[illegible] phenomenon of adsorption, whi[illegible]f a physicochemical nature. This discussion deals only with cases of the adsorption of gases by solids.

In general, every solid surface displays a certain tendency to interact with gaseous molecules that come into contact with it. This tendency can be explained by the fact that every solid surface (even the most highly polished metals) has areas of noncompensated electrostatic attraction, or unsaturated centers generated by the presence of protuberances, imperfections, or fractures.

The existence of such areas ensures that a thin layer of adsorbed molecules will be formed on the surface of the adsorbent. This layer is considered as being monomolecular—meaning that the thickness of the layer must be equal to the molecular dimensions of the adsorbed gas. This happens particularly at low pressures or at moderately high temperatures.

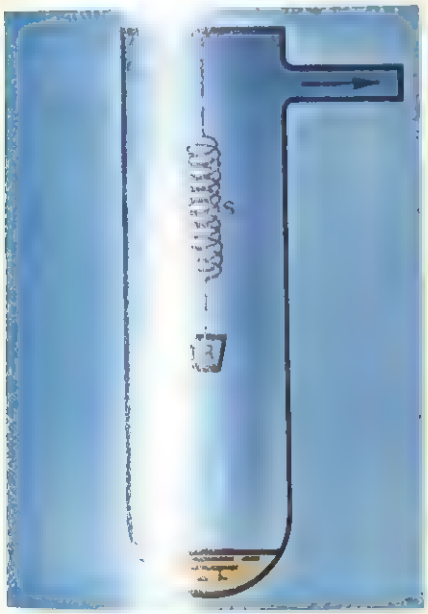
The tendency toward interaction with gases is naturally heightened when the solid is porous, because it then has a much greater surface area for a given mass or volume. A substance that has been extensively studied from this point of view, for example, is carbon in its various forms.

In view of the many aspects of adsorption that are of interest in industrial practice, these studies have now been extended to a large number of other substances. In fact, by virtue of their high adsorbent power, finely subdivided metals such as iron, platinum, nickel, and copper (and even such nonmetallic substances as alumina, clay, silica gel, and vegetable charcoal) are now used as catalysts in gaseous reactions.

Generally speaking, the two fundamental types of adsorption—physical adsorption and chemical adsorption—may be distinguished according to the types of forces that come into play. These forces between the surface and the gas molecules in the case of physical adsorption are forces of dispersion, which have only a small radius of action. These forces are rather weak and are generally known as van der Waals forces (after the Dutch physicist Johannes Diderik van der Waals). The forces that come into play in chemical adsorption are chemical in the true sense of the word. The bonds between the surface and the adsorbed molecules are rather strong (as much as twenty times as strong as the corresponding forces of physical adsorption), and in some cases they are almost as strong as the bonds existing in stoichiometric and stable chemical compounds. In addition to these two types of adsorption are cases of the mixed type, as well as more complex cases.

1

a



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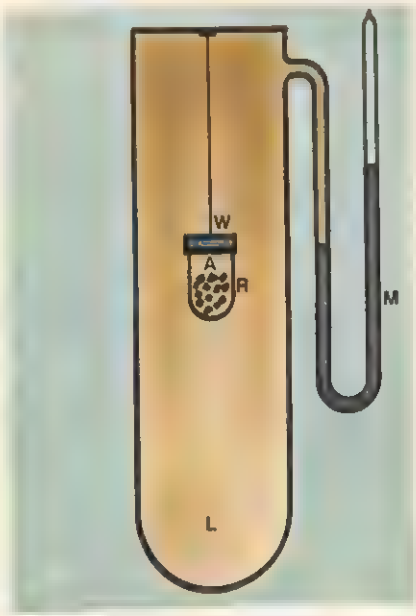



c

| Gas | Volume | Gas | Volume |
|---|---|---|---|
| sulfur dioxide | 350 | carbon dioxide | 50 |
| chlorine | 210 | methane | 15 |
| ammonia | 185 | oxygen | 8 |
| hydrochloric acid | 70 | hydrogen | 4 |

**EXPERIMENTAL MEASUREMENTS**—These illustrations represent some of the apparatus used to make experimental measurements of the adsorption of gases by solids.

Illustration 1a shows the McBain balance, which consists essentially of a small adsorbent **R** suspended from a spring **S**. The spring, normally made from a thin spiral of quartz, is calibrated in such a way that its elongation makes it possible to deduce the variations of the weight of the adsorbent **R**. The adsorbate **L**, which is in liquid form, is placed on the bottom of the apparatus. By means of suitable techniques a vacuum is created in the system, causing the liquid **L** to evaporate and become adsorbed into the adsorbent **R**. The increase in the weight of the latter enables the phenomenon to be quantitatively evaluated.

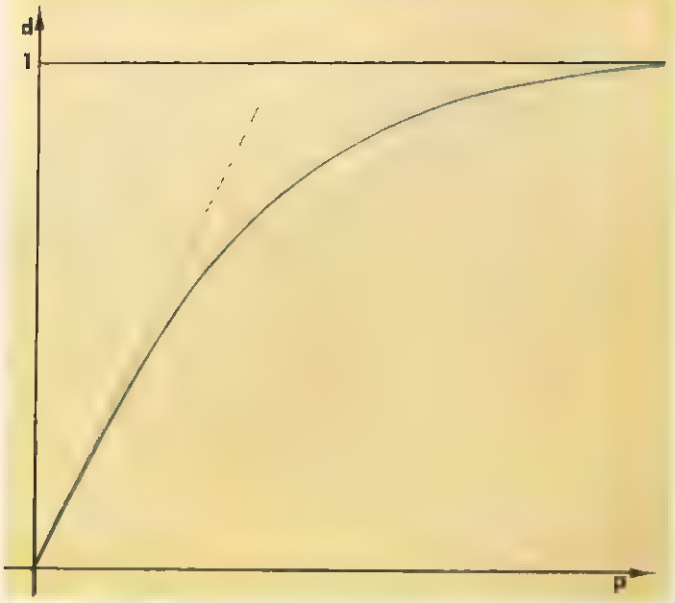
Another system in common use is shown in Illustration 1b. The large test tube contains the adsorbate **L** in gaseous form, and the pressure of this gas is measured by the manometer **M**. The adsorbent **A**, on the other hand, is kept separate in the receptacle **R**, which is closed by the magnetic top **W**. When the latter is removed, the phenomenon of adsorption takes place. The quantity of gas that is adsorbed can be determined if the volume of the apparatus is known and the decrease in pressure is measured.

Table 1c shows the volumes (in $cm^3$) of a number of gases that are adsorbed by 1 g of suitably prepared animal charcoal at a temperature of 20° C (68° F).

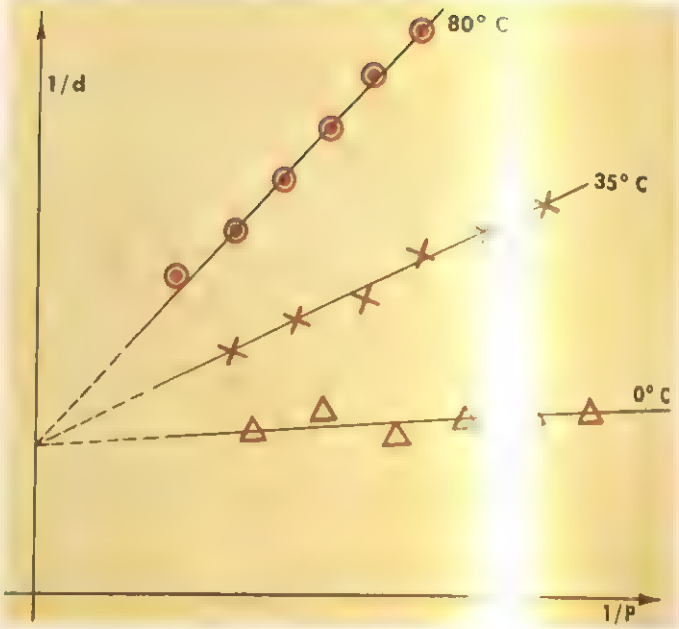
## LANGMUIR'S THEORY OF THE PHENOMENON OF ADSORPTION

The American physical chemist Irving Langmuir developed a kinetic theory of adsorption based on certain conditions of pressure and temperature. The idea behind this theory is that a situation of

2a




2b




**LANGMUIR'S EQUATION**—The graph shown in Illustration 2a represents Langmuir's equation

$$d = \frac{k_1 P}{k_2 + k_1 P}$$

The values of $d$ (ordinate) are plotted against the values of the pressure $P$. Apart from the logical observation that the surface of the adsorbent will be almost wholly covered by the adsorbate at markedly high pressures, the initial part of the curve is seen as almost a straight line; consequently, $d$ is proportional to $P$ at low pressures.

In fact, when the values of $P$ are very low, the denominator of the fraction can be simplified by the approximation

$$k_2 + k_1 P \approx K_2;$$

therefore,

$$d \approx \left(\frac{k_1}{K_2}\right) P \approx K_3 P.$$

This expression explains the almost linear form of the first part of the curve (the dotted red line is straight).

Langmuir's equation can also be written in the form

$$\frac{1}{d} = \frac{k_2 + k_1 P}{k_1 P} = \left(\frac{1}{P}\right) + 1.$$

In this form the equati… ws that a straight line is formed when 1/… otted against 1/P. Illustration 2b rec… me experimental data concerning the … otion of gaseous carbon dioxide by car… various tempera-tures. All the curves a… fact straight lines, as required by this la… m of Langmuir's equation. If the pressu… kept constant, the ratio 1/d decreases … e temperature (d increases as the temp… diminishes).

stationary equilibrium is established between a free gas and an adsorbent surface. This equilibrium is a condition in which the number of molecules adsorbed by the solid surface in a given period of time is equal to the number of molecules abandoning the surface and passing into the gaseous phase. The layer of adsorbed gas is assumed to be monomolecular. The fraction of the surface that is covered by the gas is represented by $d$, which will amount to 1 when 100 percent of the surface is covered; it will amount to 0 when the surface is wholly devoid of adsorbed molecules; and it will assume intermediate values when the surface is only partially covered. The speed with which the molecules pass from the gaseous phase to the adsorbed phase is proportional to the pressure $P$ of the gas and to the fraction of the surface $(1-d)$ that is free of adsorbed molecules. The applicable relationship is, therefore:

$$\text{speed of adsorption} = k_1 (1-d) P,$$

where $k_1$ is a constant of proportionality. On the other hand, the speed with which the molecules abandon the adsorbent is proportional to the fraction of the surface that is already covered with adsorbed molecules; therefore,

$$\text{speed of desorption} = k_2 d,$$

where $k_2$ is another factor of proportionality.

The two speeds—that of adsorption and that of desorption—must be equal when equilibrium is reached; therefore,

$$k_1 (1-d) P = k_2 d.$$

Solving this equation for $d$:

$$d = \frac{k_1 P}{k_2 + k_1 P}.$$

This equation makes it possible to calculate the quantities of gas that will be adsorbed; the values calculated in this manner agree with the data obtained from experimental measurements.

## THE DETERMINATION OF SURFACE AREAS BY ADSORPTION

Because adsorption is a surface phenomenon, it can be used to measure the total area on the surface of solid particles. The basis for this technique—called the BET technique after its discoverers, Brunauer, Emmett, and Teller—is the measurement of the amount of gas adsorbed on a solid sample as the pres… the gas is varied. This is accom… by alternately adsorbing and des… (the opposite process from adsorb… the gas at various pressures. Follo… dsorption at a measured temperatu… d pressure, the gas is desorbed and … red. From this information, the qu… ty of gas that would form a monol… ular layer covering the entire surfa… of the solid can be determined. If th… mount of gas is known, the number o… molecules necessary to cover the surface can be calculated. Therefore, the surface area may be found, providing that the area occupied by a single molecule is known. The area of the molecules to be used is usually determined precisely by other means so that accurate surface areas can be measured. As an example, the area of a nitrogen molecule is 16.3A² ($1.63 \times 10^{-15}$ cm² or about $2.5 \times 10^{-16}$ in.²).

Because many chemical reactions involving solids occur at the surface of the solid, surface area is an important factor influencing the rate of reaction. Surface areas are affected by various physical properties of a solid, especially by the average particle size and by the presence or absence of pores in the particles.

# EQUI IBRIUM DIAGRAMS | the degrees of freedom and restraints of chemical systems

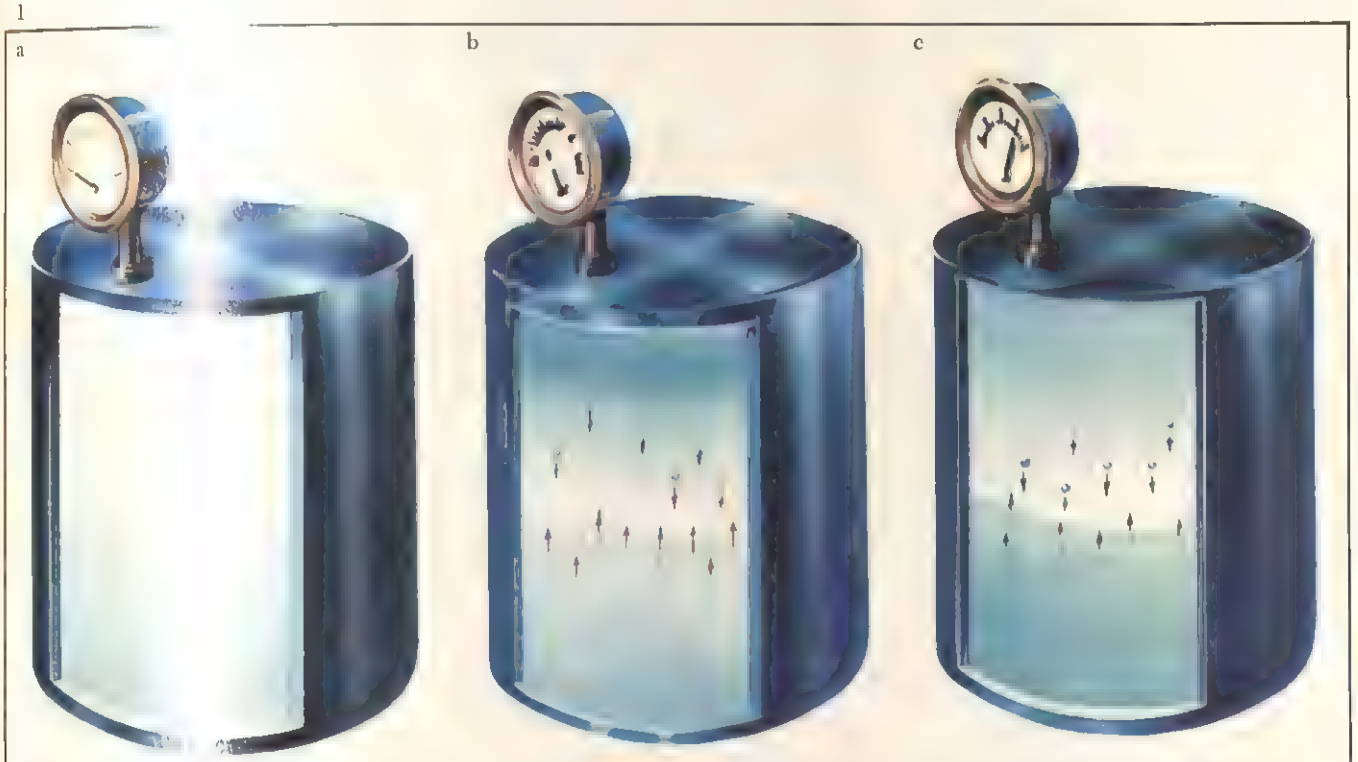
The study of eq um diagrams is of considerable in nce in numerous fields of techr and science. An equilibrium dia akes it possible to know in what r temperature, pres- sure, and conce it will be possible to obtain a cl system that pos- sesses certain characteristics that are particularly desired.

## POSSIBLE PHASES OF A SYSTEM

Because all gases can be mixed in any desired proportion, a system cannot contain more than one gaseous phase. Such is not the case in liquids, where it is possible to have phenomena of partial miscibility. In practice, this means that a system may contain several liquid phases that are in equilibrium with each other.

To observe the presence of two or

1




**EQUILIBRIUM IN . CASE OF EVAPORATION**—It is well kr . that every liquid tends to evaporate. This ency varies from liquid to liquid and beco es greater as the temperature increases hus, gasoline is far more volatile than water at ordinary room temperatures; but both gasoline and water become more volatile as the temperature rises.

The illustration shows a closed container. Initially, as shown in illustration 1a, the container is partially filled with a liquid (such as water at room temperature); above the liquid is a vacuum.

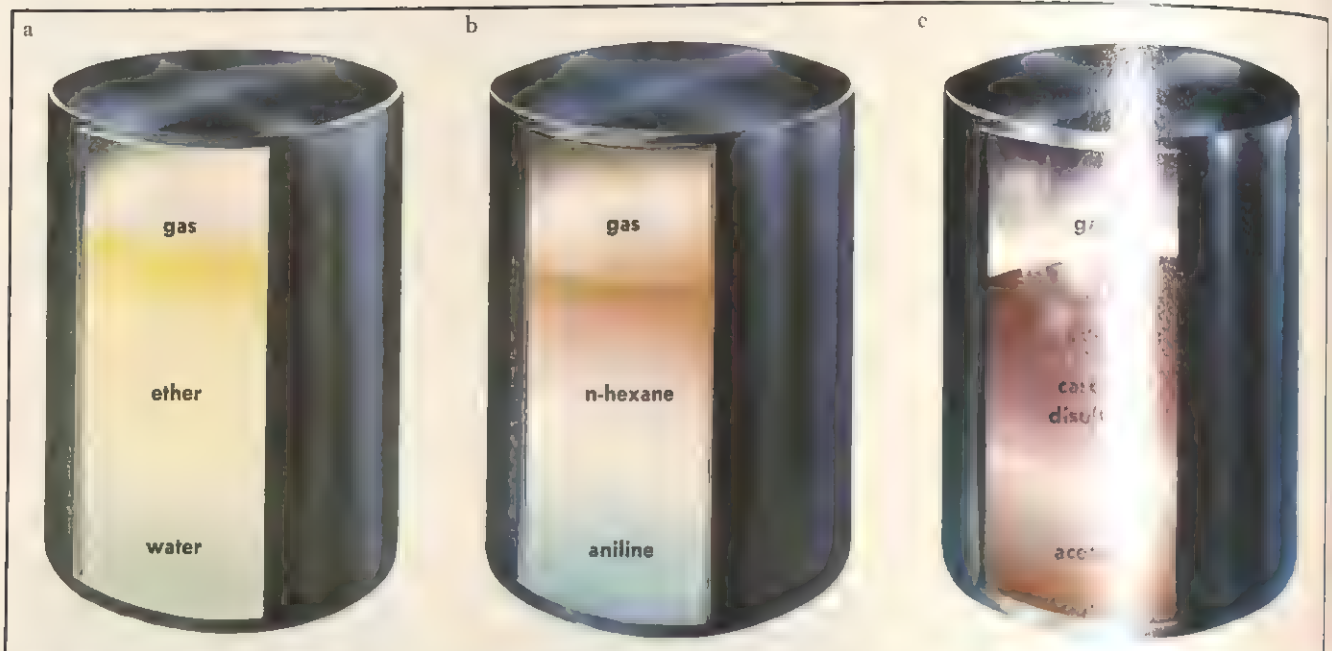
Some of the molecules of the liquid, because of their continual motion, will escape from the surface of the liquid and occupy the space at their disposal. This phenomenon of evaporation is accompanied by the inverse phenomenon of condensation, where molecules of the gaseous phase collide with the surface of the liquid and are attracted and recaptured by it (illustration 1b). Initially, with a vacuum above the water, the rate of evaporation greatly exceeded the number of molecules that recondensed. Eventually, however, the number of molecules leaving the liquid becomes equal to the number returning to it and the system within the container is in equilibrium (illustration 1c). In this state of dynamic equilibrium, the vapor above the liquid has a particular pressure, known as the saturated vapor pressure of the liquid at the temperature of the experiment. The accompanying table shows the values of the vapor pressure of water at various temperatures.

| Temperature,° C | Pressure, mm of Hg |
|---|---|
| 0 | 4.6 |
| 10 | 9.2 |
| 20 | 17.5 |
| 30 | 31.8 |
| 40 | 55.3 |
| 50 | 92.5 |
| 60 | 149.4 |
| 70 | 233.7 |
| 80 | 355.1 |
| 90 | 525.8 |
| 100 | 760.0 (1 atmos.) |

That the vapor pressure of a liquid varies with the temperature is easily explained. The liquid consists of molecules in continuous random movement. The speed of their movement increases as temperature increases. In spite of the attractive forces that tend to keep molecules together, increased speed of movement results in an increased number of molecules entering the gaseous phase. As their numbers increase, however, so does the number of collisions with the surface of the liquid, and the probability of recapture into the liquid correspondingly increases.

These considerations show that temperature is an important factor in determining the equilibrium conditions of evaporation of a liquid. The example presented in this illustration shows the concept of equilibrium between the different phases of a system. (Each phase, of course, is here considered to be a homogeneous and physically distinct part of a more complex system.) Two phases are shown in this illustration; they are the liquid phase and the gaseous phase.

2




**SYSTEMS WITH PARTIAL MISCIBILITY IN THE LIQUID STATE**—This illustration shows three different examples of substances that are characterized by a partial miscibility. This phenomenon occurs only when the substances are in the liquid state. When the substances are in the gaseous state, they can be mixed in any desired proportions. In the liquid state, the system consists of several liquid phases in equilibrium; in the gaseous state, only one phase is possible—a mixture of gases.

Illustration 2a shows a system consisting of ether (the upper l id water. Illustration 2b shows a syste p of normal hexane (the upper layer) a niline. Illustration 2c shows a system fo by carbon disulfide (the upper layer) ar tone.

more phases in a liquid, that liquid must remain at rest for a certain period of time. The formation of two or more layers—whose separation line corresponds to the separation line of the phases—will then be seen. (Illustration 2 shows a number of such cases.)

In the case of solids, each solid normally constitutes a phase of its own; nevertheless, it is comparatively easy to obtain the formation of mixed crystals (or solid-state solutions) of two or more substances—solutions that must be considered as a single solid phase.

Moreover, certain substances can exist in two or more forms (crystal structures) that differ from each other (allotropic forms). Each allotropic form must be considered as a phase of its own. On the basis of this statement, the equilibria between the various phases that have been mentioned can be predicted. Thus, when a system consisting of a single component is considered, the solid-liquid equilibrium will correspond to the phenomenon of melting, the liquid-vapor equilibrium will correspond to the phenomenon of evaporation, and so forth.

## COMPONENTS AND DEGREES OF FREEDOM OF A SYSTEM

A component is either an element (such as zinc or aluminum) or, more frequently, a chemically defined compound (such as water, alcohol, or sodium chloride).

A component may be present in different forms. More precisely, it may be distributed in different phases. For example, in a system consisting of water in the form of steam, liquid water, and ice, the same component, $H_2O$, is distributed in three different phases.

A system may be made up of either one component or of several. Simple systems, in which the number of components is either one or two, are the easiest to understand.

The concept of the degrees of freedom, or the variance of a system (the latter term is more commonly used to indicate the degrees of freedom of a system) is more complicated.

The degrees of freedom of a system are given by the number of variables that can be modified without changing the number of ph equilibrium. In practice, the va f primary interest are temperatur re, and composition (when th consists of two or more component the system. In order to clarify th pt of the degrees of freedom, Illus 3 shows a system consisting of a s mponent (water) distributed in th ses. The only variables in this syst e the temperature and the pressu

## THE PHASE RU

The phase rule makes it possible to predict the number of phases that can remain in equilibrium in certain conditions. This rule, also called Gibbs's rule after the American mathematical physicist Josiah Willard Gibbs, states that the number of phases in equilibrium in a given system is equal to the number of the components increased by two and diminished by the variance of the system. The algebraic form of the rule is

$$F = C + 2 - V, \qquad (1)$$

where $F$ is the number of phases in equi-

librium, $C$ the nu[illegible]er of components, and $V$ the varian[illegible] or the number of degrees of freedo[illegible] the system.

Inasmuch as th[illegible]imum value of $V$ is zero, the maxi[illegible]lue of $F$ may be obtained by

$$F = 1 \quad 0 = 3$$

for systems with [illegible]mponent, and by

$$F = \quad 0 = 4$$

for systems wit[illegible]omponents.

In a system c[illegible] of a single component there ca[illegible]erefore, be more than three phase[illegible]ilibrium; in a system consisting [illegible]components there can be a maxi[illegible] four phases in equilibrium, and [illegible]th.

If the numbe[illegible]nponents and the number of pha[illegible] equilibrium are known, the vari[illegible] a system may be obtained from a rearranged form of equation (1):

$$V = C + 2 - F. \qquad (2)$$

In fact, the phase rule is often expressed in this latter form.

For example, in the case shown in Illustration 3a (one component, three phases in equilibrium)

$$V = 1 + 2 - 3 = 0$$

is obtained. This is known as an invariant system. In the case shown in Illustration 3b, on the other hand,

$$V = 1 + 2 - 2 = 1$$

is obtained. This is known as a monovariant system. In the case shown in Illustration 3c,

$$V = 1 + 2 - 1 = 2$$

is obtained, and this is known as a bivariant system.

The phase rule is limited in its application to the behavior of systems assumed to be subject only to variations in pressure, temperature, and proportions of components, and free from influences of electrical and magnetic fields, of gravitational effects, and of surface energy effects. The effect of gravity, which can practically never be eliminated, is altogether negligible for almost all applications of the phase rule. Surface effects, on the other hand, are extremely important in systems containing finely divided colloidal substances or other materials possessing large surfaces, such as adsorbents and catalysts. The interphase relations in these cases are not covered by the ordinary phase rule, which applies to equilibrium of bulk phases.

3

**VARIANCE AND D[illegible] OF VARIANCE**—Illustration 3a shov[illegible] phases of water—vapor, liquid, and [illegible]in equilibrium. This is possible unde[illegible]cise temperature of 0° C (32° F) and [illegible]rticular pressure of 4.6 mm of mercu[illegible]e temperature were varied and the [illegible] kept constant with the help of a m[illegible] the ice would melt over 0° C, or th[illegible] would freeze below 0° C. Similarly, i[illegible]nperature were kept constant and the [illegible]e varied, one of the three phases wo[illegible]ppear. The variance of the three-pha[illegible]m shown in Illustration 3a is, there[illegible]o. The system is invariant. Neither t[illegible]re nor pressure can be changed without one of the three phases disappearing.

Illustration 3b shows an example of the evaporation equilibrium of water—the liquid phase and vapor phase in equilibrium. The table presented in Illustration 1 shows the very precise relationship required between temperature and pressure in order to retain equilibrium. From this, the assumption could be made that if the temperature were kept constant—for example, at 50° C (122° F)—and the pressure were varied either above or below its equilibrium value (92.5 mm of mercury), the disappearance of either the gaseous phase or the liquid phase would result. Such, however, is not the case. The system shown consists of one component in two phases, wherein the variance equals one—a monovariant system. In fact, then, it is possible to vary one of the variables (either temperature or pressure) without causing the disappearance of one of the two phases (liquid and vapor) in equilibrium.

Illustration 3c shows a system consisting solely of water vapor. In this case, it is possible to vary both the temperature and the pressure (within limits) without varying the phase of the system. The variance of this system is, therefore, two; it is a bivariant system.

a

b

c

# SOLUTIONS | homogeneous connections between molecules

The Earth spins through space, its atmosphere held in place by gravity. The Earth's atmosphere is made up of gas dissolved in gas—a solution. A plane

1

**ZINC AND SULFURIC ACID**—Although zinc reacts with sulfuric acid and dissolves completely, the process is one of reaction, not solution. Subsequent evaporation does not produce metallic zinc.

speeds through a cloud, a car inches its way through fog—both are moving through a liquid dissolved in gas—in each case, a solution. A house catches fire, smoke diffuses into the air; a solid is dissolving in gas, which is also a solution.

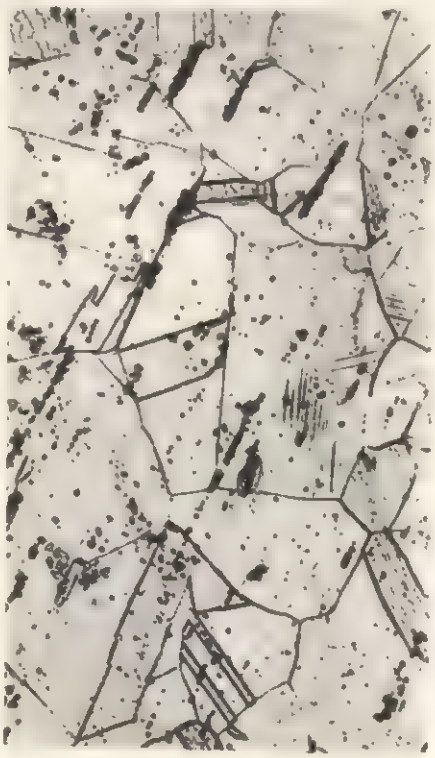
A solid dissolved in a liquid, or in another solid; a gas dissolved in a gas; a liquid dissolved in a liquid; or any combination of these is a solution. In a solution, the component that is present in greater quantity is the solvent. The one present in a lesser quantity is the solute. Solutions are homogeneous mixtures of a number of components. There is an important difference between homogenous and heterogeneous mixtures. Two examples that point up this difference are the common alloys brass and steel. At first glance, both might be mistaken for homogeneous mixtures and so taken to be solid solutions. But closer observation of the crystal lattices of the two alloys is most revealing. Brass is an alloy of copper and zinc. It has a face-centered-cubic crystal structure in which some zinc atoms have replaced copper atoms. Because one of the elements forming the alloy has penetrated into the crystalline structure of the other without modifying the characteristics of the structure and in such a way that the crystals present are always of a single type, the mixture is considered homogeneous. The term homogeneous, however, cannot be applied to steel. Steel is an alloy composed of iron, carbon, and a number of other elements, such as silicon, manganese, titanium, chromium, vanadium, and others. Except for those instances when iron and carbon mix homogeneously, steel is made up of crystals of various combinations that join in a heterogeneous mixture. Because the essential co ion of homogeneity is lacking in the l alloy, it cannot be considered a solution.

The difference bet a solution and a pure solvent can b rved by studying the effect of the ion of a solute to a solvent. If a sm iece of zinc is placed in sulfuric a a short time the zinc will dissolv letely. If what remains is heated an liquid evaporated, the metallic z ll not again be present. This is, ther not a solution of two components ather a totally new substance. Th mical reaction that took place is as s:

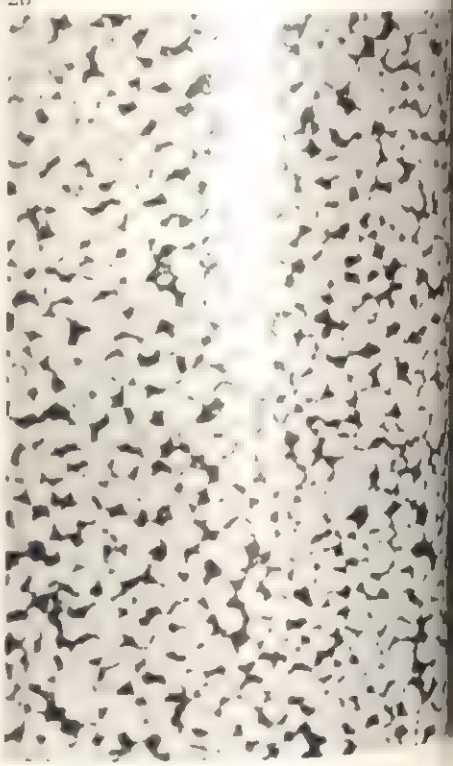
$$Zn + H_2SO_4 \longrightarrow SO_4 + H_2.$$

**HOMOGENEITY AND HETEROGENEITY**—If a mixture is to be a solution, it must be homogeneous. At first sight, the two common alloys, steel and brass, seem homogeneous. Under the microscope, however, steel (Illustration 2a) is revealed as a heterogeneous mixture of iron, carbo (magnification 200 X). I a homogeneous struct atoms have replaced copper's crystalline 250 X).

2a



2b



l other elements Illustration 2b) is cause some zinc r atoms in the e (magnification

A requirement
therefore, is tha
undergo no ch
must remain un
tion of the liqui

Note the foll
A glass filled wi
second glass fil
water and salt
enclosure. Even
is seen to drop

solution process,
lissolved substance
alteration, and it
after the evapora-

simple experiment.
water (A) and a
ith a solution of
placed in a glass
he level in glass A
level in Glass B

rises. The molecules pass through the vapor stage from the pure solvent to the solution; that is, the pure water has a stronger tendency to evaporate than does the solution. The solute lowers the solvent's vapor pressure. It is considerably more difficult for the water molecules to escape from the solution because they are involved in the mutual forces of attraction, however weak, with the dissolved particles. To escape from the liquid, the molecules must overcome the new forces created by the introduction of the solute in the solvent, forces beyond normal intermolecular forces. This can be confirmed in a variety of experiments.

The solutions discussed thus far are those in which a solute has been added at random to a given solvent. These solutions have been unsaturated—as solutes have been added, the solutions have continued to dissolve them. When an added

**SOLVENTS AND**
adding a solute t
in this simple ex
placed under a gl
is filled with a sol

**ES—The effects of**
nt can be observed
t. Two beakers are
ver. The first beaker
f copper sulfate, and

the second with pure water (Illustration 3a). Although the levels of the two liquids were equal initially, the level of the water becomes lower than the level of the copper sulfate (Illustration 3b). Molecules have passed through the vapor stage from the pure solvent to the solution. The water molecules in the solution are impeded in leaving the solution by the mutual forces of attraction with those of the solute.

3a

3b

4a

4b

**UNSATURATED AND SATURATED SOLUTIONS**—By adding a solute to a solvent, an unsaturated solution results (illustration 4a) as long as the solute dissolves. When a solute is added and no longer dissolves, a saturated solution occurs (illustration 4b).

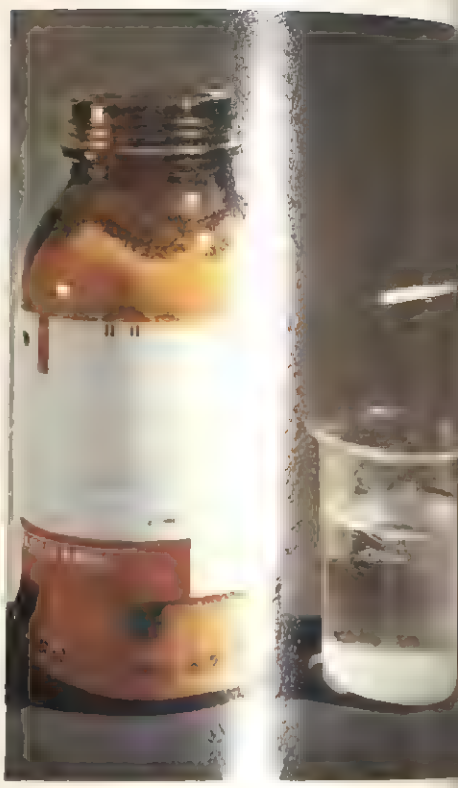
solute does not dissolve but remains in its solid state in equilibrium with the solution above it, a saturated solution results. The concentration of a saturated solution clearly represents the solubility of the solute in that particular solvent. The equilibrium established between a solution and a dissolved solute may appear to be static, but in fact is dynamic—for the process of solution is a continual one, with the solution depositing an amount of solute equivalent to the amount absorbed. In any interval of time, the particles passing into solution are equal in number to those being simultaneously deposited by the solution itself. Consequently, there is a continual movement of particles that does not alter either the concentration of the solution or the weight of the solute in equilibrium. It is important to note that it is not necessary to have excess solute to have a saturated solution; if the excess solute floating in the solution is filtered out, a saturated solution will result. Even if some other solute were added, an equal amount of it would still be deposited.

When a solute dissolves in a solvent, enough energy must be supplied to break the bonds between the molecules of the solute. The same is true of the solvent because its molecules must overcome the forces between them in order to make room for the molecules of the solute.

**SATURATED SOLUTIONS**—If a solution in which part of the solute is in the solid state is filtered, a saturated solution will result. If more solute is added, an equal amount of it will be deposited.

5

6



**THE EFFECT OF A CO** **ION**—The effect of a solute in solutio solubility of another solute is gen gligible, except when the two solutes ntain the same ion. In this case, the of the second solute diminishes th ty of the first. The illustration show ion of NaCl and KCl.

The system provid rgy when the particles of the sol nd the solvent attract each othe mplete picture of solubility may b ined when the influences exercised i e nature of the solute and the solv by temperature and by pressure, are sidered.

The solubility of the solute is greater in polar solvents ($H_2O$) for ionic compounds than for the others. For example, sodium chloride dissolves in water in greater quantities than does sugar. The crystal lattice of sodium chloride, unlike that of sugar, is made up of ions which, because of their charge, attract water molecules. Because these molecules contain positive and negative poles, they are attracted by the ions electrostatically, surrounded, and split off from the crystal.

It is interesti · note that the effect of a dissolved s · n another solute in the same solution · ost negligible, except when the tw · ites both contain the same ion. If · is dissolved in water and KCl is · the solubility of the sodium chlo · iminishes noticeably. The nature · olute is, therefore, of great import · solution processes.

Various s · have different behavior patterns · lear that the more similar the · to the solute, both structurally · ectrically, the easier it will be fo · ion to form. A polar solute like · will dissolve more easily in a · with similar characteristics (wa · example) than in a nonpolar sul · In the case of solid solutes, a · vent will have the greatest effe · nic compounds, such as common · lt (NaCl).

The influ · temperature on the solubility of · or solids cannot be generalized · may be stated that when a gas · lved in water, solubility diminis · mperature increases. This proces · be compared to air bubbles rele · water as water is heated but b · boils. To understand what happe · solubility of solids and liquids · perature varies, the solution heat · t developed when a solute dissol · orms a saturated solution) must · dered. This heat can be estimated · imentally and may be either positi · negative. Some substances produ · at when they dissolve. Others require · at in order to dissolve. The heat, pos · or negative, depends on two distinct · nds of energy involved in the process of solution. Energy is needed to break the solute's crystal lattice (the reticular energy), and energy is generated during the hydration of particles by the solvent's molecules (the hydration energy). The solution heat clearly depends on the relative value of these two types of energy. If reticular energy is less than hydration energy, the process is exothermic, and solution heat is positive. If hydration energy is greater, then the process is endothermic, and solution heat is negative.

From the foregoing it is obvious that temperature does exert an influence in the solution process. For example, consider a saturated solution of a generalized salt, called AB, in equilibrium with solid salt according to the reaction:

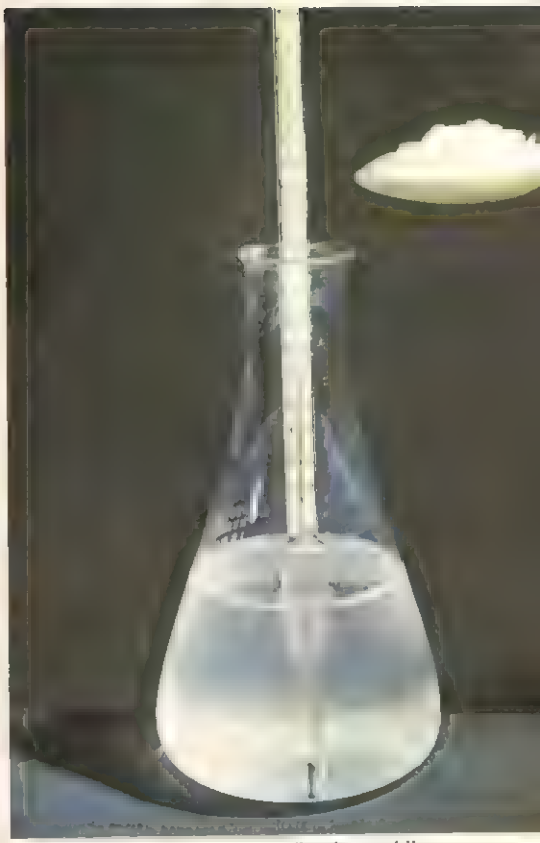
$$AB + H_2O \rightleftarrows \text{solution}.$$

In this hypothesis, heat is needed to obtain the solution; that is, the process is endothermic, and the reaction towards the right will only take place if a certain quantity of energy is provided. The reaction in the opposite direction will obviously be exothermic and will develop heat. As indicated, the equilibrium is dynamic; the two processes occur continually, with the solid dissolving and reprecipitating. If heat is now applied, the additional energy will disturb the equilibrium and favor the endothermic solution process. AB will dissolve more quickly than it is reprecipitating until a new equilibrium is reached with more of the solid solute in solution. In this case, therefore, providing more heat means increasing solubility.

Pressure has no special influence on the solubility of solids or liquids. The solubility of gases, however, increases with an increase in pressure. For example, if the top of a bottle of water in which carbon dioxide has been dissolved at high pressure is removed, the pressure drops and the carbon dioxide bubbles off because its solubility is now much lower.

7a

7b



**THE EFFECT OF TEMPERATURE**—Temperature has an effect on the solubility of liquids and solids. The solution heat (the heat developed when a solute goes into solution) must also be taken into consideration. This heat may be negative or positive because some substances require heat to dissolve, while others create heat in dissolving. In illustration 7a, copper sulfate is dissolving as it is heated. In illustration 7b, potassium hydroxide (KOH) is dissolving in water and producing heat.

# SINGLE-COMPONENT SYSTEMS | equilibrium diagrams for water and sulfur

Consider systems consisting of a single pure component. The physical states of all such systems are completely defined if the temperature and pressure of the system are known. Moreover, the system can be described graphically by phase diagrams that show the range and the limits of stability of the various phases.

In the case of single component systems this is a rather simple task because it is not necessary to take into account other variables such as chemical composition. In fact, all that is needed is a graph in which equilibrium temperature is plotted against pressure. Such a graph shows immediately the temperature and pressure conditions under which the individual phases are stable.

Graphs of this type are called phase diagrams. Following are some examples of single-component systems.

## WATER

Under normal conditions (room temperature and a pressure of 760 mm of mercury), water is a colorless, tasteless liquid with the following physical characteristics.

PHYSICAL CONSTANTS OF WATER

| | | |
|---|---|---|
| | melting point | 0° C |
| | boiling point | 100° C |
| specific gravity | of water at 0° C | 0.99987 |
| | of water at 4° C | 1.00000 |
| | of water at 20° C | 0.99820 |
| | of ice at 0° C | 0.9167 |
| latent heat of fusion at 0° C | | 1,429 cal/mole |
| latent heat of vaporization at 100° C | | 9,704 cal/mole |

To construct a phase diagram for water, it is convenient to begin by treating separately the evaporation equilibrium (liquid-vapor), the sublimation equilibrium (solid-vapor), and the melting equilibrium (solid-liquid). Each of these equilibria is governed by the Clapeyron equation (named for B. [illegible] Clapeyron):

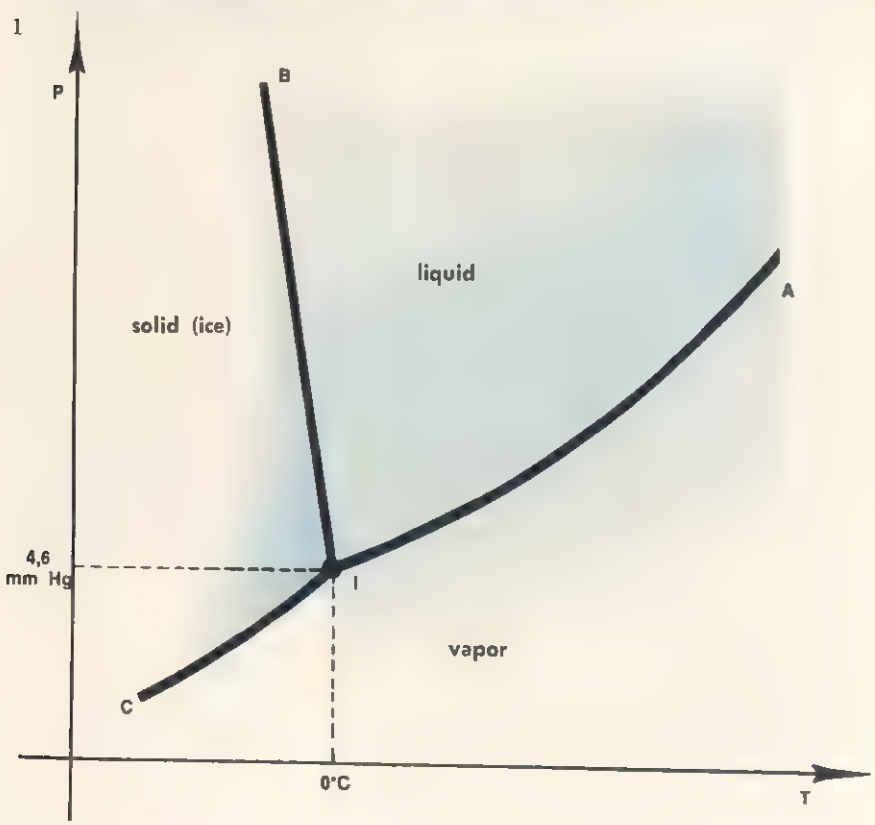
$$\frac{dP}{dT} = \qquad (1)$$

in which $dp/dT$ rep[illegible] the rate of increase of the press[illegible] with respect to the temperature, $\Delta$[illegible] e heat needed to convert one gr[illegible] lecular weight (mole) of water ([illegible] ms) from one phase to another (in [illegible] se of evaporation, for example, $\Delta$ [illegible] the latent heat of vaporization; tha[illegible] ic heat needed to convert one mol[illegible] water from the liquid phase to the [illegible] phase) at the absolute temperatu[illegible] bsolute temperature $T$ = degrees [illegible] grade + 273.2), and $\Delta V$ is the chang[illegible] gram-molecular volume that tak[illegible] e when evaporation, sublimation [illegible] sion occurs. In the case of evaporati[illegible] example, curve IA (Illustration [illegible] hich represents equilibrium betwe[illegible] liquid and vapor phases, can b[illegible] tructed in two ways. The first [illegible] of using the Clapeyron equatio[illegible] iculate the rate of increase of th[illegible] pressure at all temperatures. This [illegible] ly be done, of course, if the latent [illegible] f vaporization at all these temper[illegible] is known. The second method is [illegible] ental. It consists of measuring t[illegible] sures that correspond to a serie[illegible] aporation temperatures. For ex[illegible] a pressure of 760 mm of mercu[illegible] e atmosphere) corresponds to a te[illegible] ture of 100° C; this is the normal b[illegible] point of water.

The liquid-vapor [illegible] ve shows very clearly that the boil[illegible] point of water varies with atmosph[illegible] pressure. To be more precise, water boils at higher temperatures as pressure increases. Two well-known examples illustrate this phenomenon. The first refers to cooking in the mountains. Water boils at less than 100° C at high altitudes; its boiling point has decreased as a result of lower atmospheric pressure. Th[illegible] second refers to pressure cookers. In a pressure cooker the water remains in the liquid phase at temperatures above 100°C because higher pressure has produced an increase in the boiling point.

The sublimation equilibrium of water is represented by curve IC in Illustration

**THE PHASE DIAGRAM OF WATER**—The curve **IA** separates the liquid and vapor phases at the temperature and pressure points indicated. **IC**, on the other hand, separates the solid phase from the vapor phase, and **IB** the solid phase from the liquid phase. The three phases coexist at the point **I**, which is common to all three curves.



1. This curv parates the solid phase (ice) from por phase. The sublimation curv rsects with the evaporation curv point I. At this point, therefore, t uid, solid, and vapor phases coex this reason, the point is called the point of the substance.

Finally, th ing equilibrium is represented by IB. This curve is almost vertica use the melting point of water v ly a little bit with changes in a heric pressure. It is interesting to however, that in the case of wate rease in pressure lowers the melt point. In this respect, therefore, cu B differs from curves IA and IC. In IA and IC an increase in pressure ompanied by an increase in the brium temperature.

At this poi gram-molecular volume, $\Delta V$, co to play. In the case of melting equi the value of $\Delta V$ is given by

$$\Delta V = V_{\text{liquid}} - V_{\text{solid}} \qquad (2)$$

where $V_{\text{solid}}$ liquid are the volumes occupied by m-molecular mass of water (18 g) in the solid and the liquid phase ctively. In the case of water,

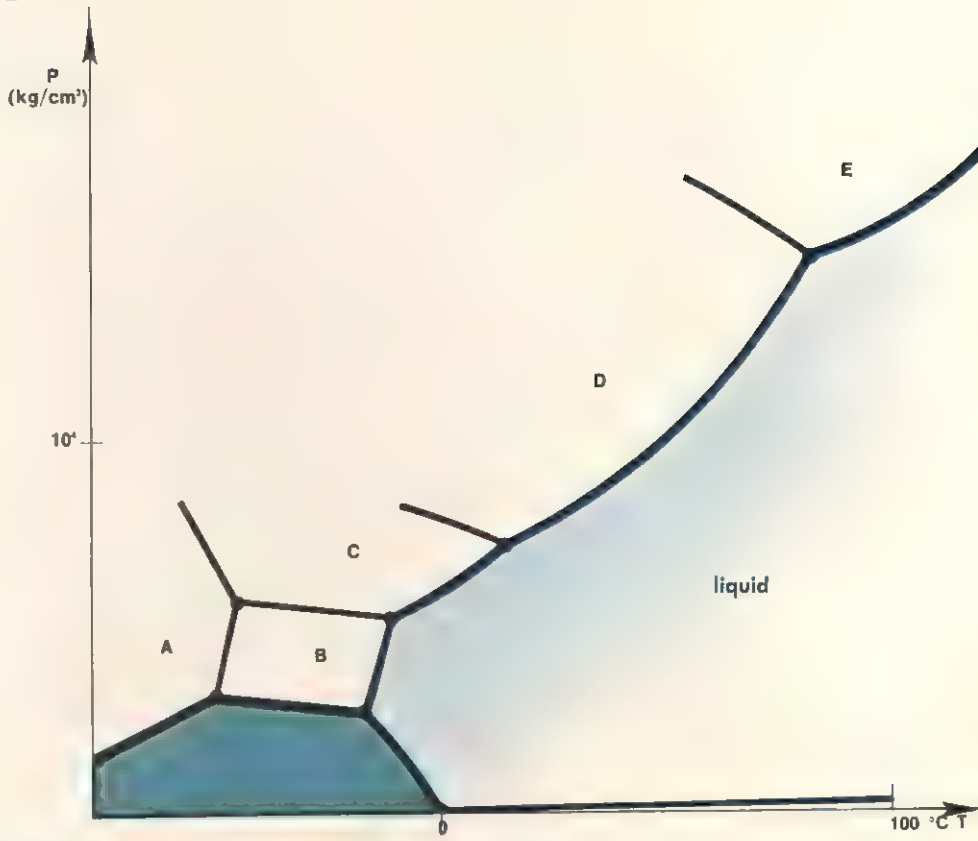
$$V_{\text{solid}} > V_{\text{liquid}}. \qquad (3)$$

Thus, the sp gravity of ice is less than the sp gravity of water (see table) and i ts on water.

It follows equation (2) that under these cir ances $\Delta V$ must be negative. Again reference to water, if both $T$ and $\Delta H$ are positive, then the value of $dP/dT$ must be negative. In other words, the pressure must decrease as temperature increases, and vice versa.

This particular aspect of the behavior of water is unique. Very few other substances behave in a similar manner.

Now examine the entire phase diagram of water. Note that it consists of areas that describe the range of stability of individual phases; equilibrium curves that define the limits of these areas and establish the various points at which different phases can coexist; and finally, a point that is defined by the intersection of the three equilibrium curves.




**THE PHASE DIAGRAM OF WATER AT VERY HIGH PRESSURES**—The green area represents normal ice (ice crystallized in hexagonal form). The areas **A**, **B**, **C**, **D**, and **E** represent the various other crystalline forms ice can assume in the solid state.

The phase diagram of water at high pressures is actually more complex than shown here, because the curves have been somewhat simplified.

According to the phase rule (discussed in a previous article), the variance of the system is expressed by the following relationship:

$$\text{variance} = \text{number of components} - \text{number of phases} + 2. \qquad (4)$$

In each of the three areas of the water phase diagram, therefore, this works out to $V = 1 - 1 + 2 = 2$. The system is, therefore, bivariant in these areas. Along the curves, on the other hand, $V = 1 - 2 + 2 = 1$, and the system is monovariant. Finally, at the point I (the triple point), $V = 1 - 3 + 2 = 0$; the system is invariant.

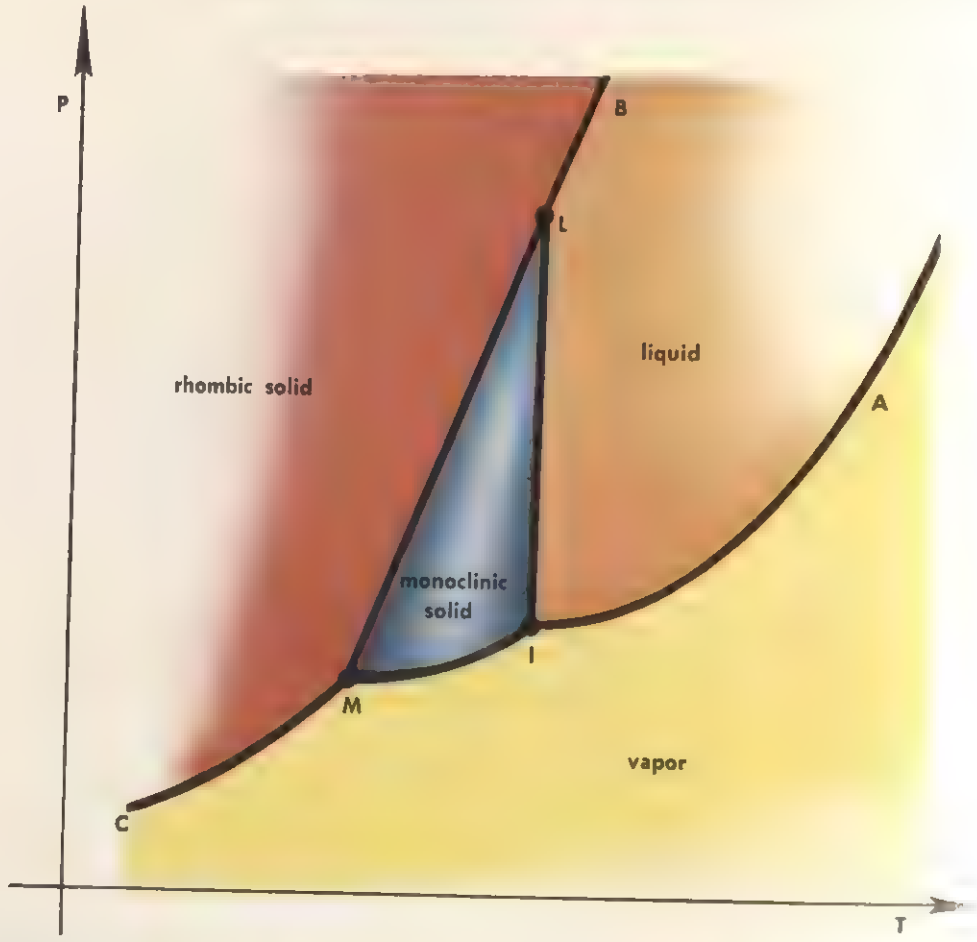
The coordinates at the triple point I are: pressure = 4.6 mm of mercury and temperature = 0° C (to be more precise, the value of the temperature at the triple point is 0.0097° C). The phase diagram of water has also been studied at very high pressures. Under these conditions ice displays crystalline forms that are different from the stable hexagonal structure found under normal conditions. Illustration 2 shows schematically the phase diagram of water up to a pressure of 10,000 kg/cm². This gives some idea of the complexity of the system.

## SULFUR

The phase diagram of sulfur is more complex than that of water at low pressures (see Illustration 1). In fact, sulfur can exist in two different crystalline forms —the rhombic form and the monoclinic form. A simplified phase diagram for sulfur is shown in Illustration 3. This diagram consists of the following:

1) The curve CM, the sublimation curve for rhombic sulfur.
2) The curve MI, the sublimation curve for monoclinic sulfur.
3) The curve IA, the vaporization curve for liquid sulfur.
4) The curve ML, which represents the transition between rhombic and monoclinic sulfur.
5) The curve LB, which represents the melting of rhombic sulfur.

3




**THE PHASE DIAGRAM OF SULFUR**—This single-component system consists of four phases (rhombic sulfur, monoclinic sulfur, liquid sulfur, and sulfur vapor). Sulfur is rhombic below 96° C (204.8° F) and monoclinic between 96° C and 119° C (246.2° F). The two solid forms and the vapor coexist at the triple point **M**. Similarly, the vapor, the liquid, and t noclinic solid co- exist at point **I**. The po is the triple point of the liquid and the t id forms.

6) The curve IL, which represents the melting of monoclinic sulfur.

The sulfur system is monovariant along each of these curves.

This phase diagram consists of four areas corresponding respectively to two solid phases, the liquid phase, and the vapor phase. Within each of these areas the system is bivariant.

There are also three triple points I, L, and M. At these points the system is invariant.

It should be pointed out that the phase diagram in Illustration 3 is not drawn to scale, and must, therefore, be regarded as a qualitative description of the system. The upper part of the pressure scale has been greatly compressed in order to show all of the stable phases within a reasonably small space.

The sulfur system lends itself to an interesting application of the phase rule (4). Suppose it is desirable to find out if there is a point in the sulfur phase diagram where the four phases (rhombic, monoclinic, liquid, and vapor) coexist in stable equilibrium. Using the phase rule (4) to determine the variance of the system under these conditions, the result is

$$V = 1 - 4 + 2 = -1.$$

In other words, the variance of the system would be negative. This result is absurd, however; hence it can be safely stated that such a point cannot exist. It is, therefore, not possible to have more than three of the four phases in simultaneous equilibrium. The table below shows the coordinates of the triple points in the phase diagram of sulfur.

COORDINATES OF THE INVARIANT POINTS OF SULFUR

| | | |
|---|---|---|
| 1) point I | $t = 119°$ C, | $P = 0.00004$ atmospheres |
| 2) point L | $t = 154°$ C, | $P = 1{,}400$ atmospheres |
| 3) point M | $t = 96°$ C, | $P = 0.00001$ atmospheres |

The actual physical and chemical properties of a substance are not directly indicated on the phase diagram, but they are nontheless completely determined by information in the diagram.

# TWO COMPONENT SYSTEMS | liquid-solid equilibria

Numerous sys… consist of two components. This … however, considers only those eq… that can be established betwe… d and solid phases.

The total … of variables in a two-compone… n is three: the temperature, the … re and the percent composition o… stem. As a result, complete equ… diagrams for two-component sy… re rather complex. They require a … dimensional coordinate system, w… h of the three coordinates repres… one of the variables. To avoid this … dimensional graphic representation … the three variables can be regarde… constant, permitting study of the pl… uilibria of the other variables in a … mensional graph.

For this r… the phase diagrams of this article … e a fixed value for pressure (one … phere). This allows study of solid … phase equilibria in terms of temp… re and composition alone. In othe… ds, a constant pressure of one at… ere (760 mm of mercury) is assu… nd the variation of crystallization … erature may be studied in terms o… composition.

The phase … already discussed in previous artic… as follows:

variance = … er of components − n… of phases + numbe… hysical variables

For the ex… considered here (P = constant) thi… le becomes

$$v = 2 - \phi + 1 = 3 - \phi \qquad (1)$$

This relationship shows that the number of phases $\phi$ in equilibrium cannot exceed three. With three phases the system will be invariant ($v = 0$).

Numerous types of equilibrium diagrams are used. In this article, however, only the most important and simplest ones are discussed. Moreover, only those equilibria in which the two components are completely miscible in the liquid phase will be treated.

## PHASE DIAGRAMS WITH THE COMPONENTS COMPLETELY IMMISCIBLE IN THE SOLID PHASE

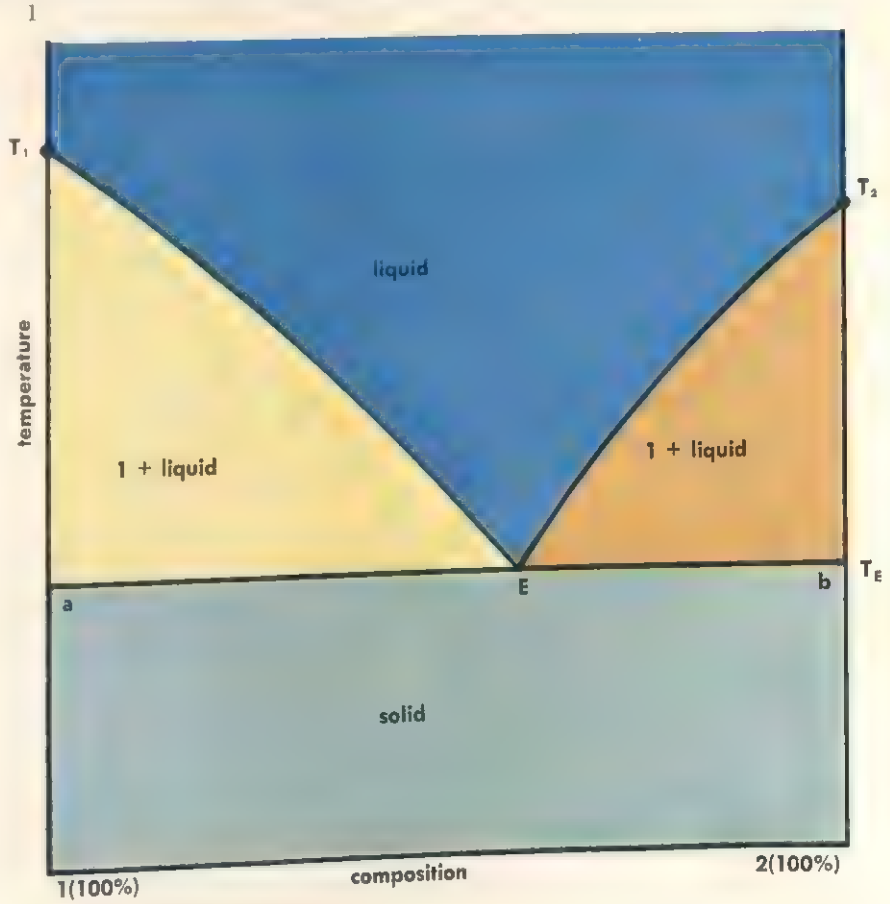
*Systems without intermediate compounds*—The phase diagram applicable in this instance is shown in Illustration 1. There are two components (1 and 2); these components melt respectively at temperatures $T_1$ and $T_2$. Mixtures of these two substances, however, melt along the curve $T_1ET_2$. This curve is, therefore, known as the liquid curve. The point $E$ is called the eutectic point (eutectic is derived from the Greek for "which melts easily"); the corresponding temperature $T_E$ is called the eutectic temperature. The system is completely solid below the straight line $aEb$; it is completely liquid above the curve $T_1ET_2$. In area $T_1Ea$ crystals of substance 1 are in equilibrium with the liquid, while in area $T_2Eb$ the liquid is in equilibrium with crystals of substance 2.

The solid that separates from the liquid phase at point $E$ consists of an intimate mechanical mixture of the crystals of substances 1 and 2. This mixture is called the eutectic mixture. It must not be confused with a chemical compound, for it does not have the characteristics of a true compound.

Solids crystallizing below the straight line $aE$ consist of crystals of substance 1 plus the eutectic mixture. Similarly, below line $bE$ the crystallizing solids will consist of crystals of substance 2 plus the eutectic mixture.

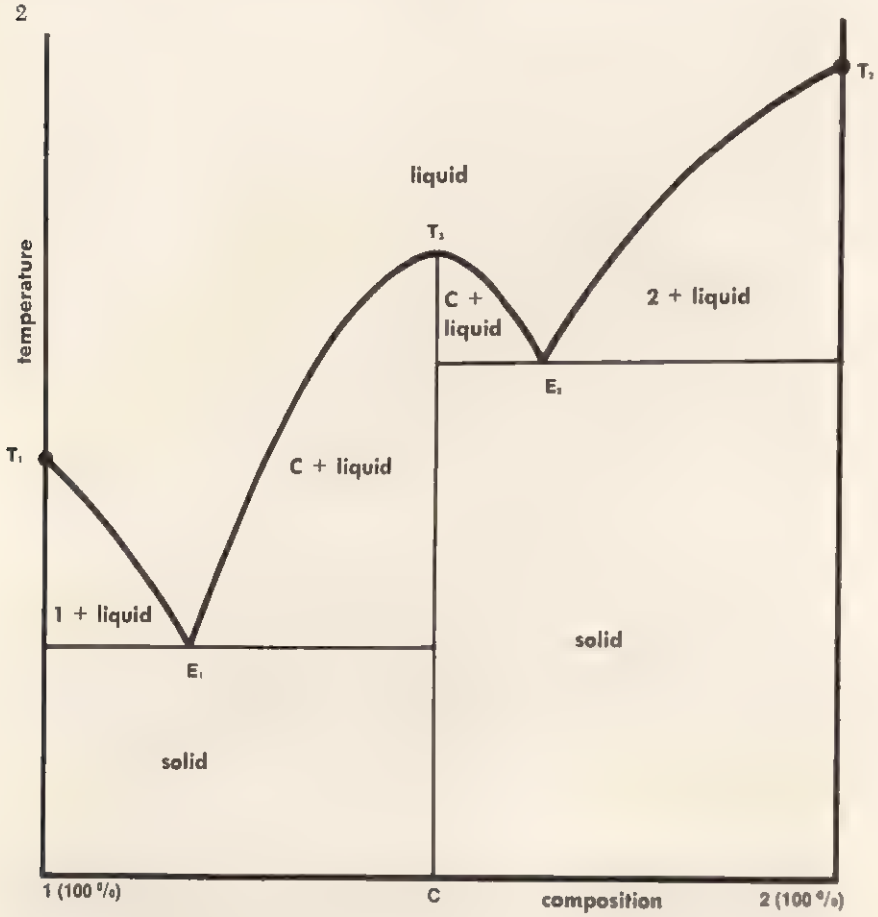
It is interesting to note that the addi-

**SYSTEMS WITHOUT INTERMEDIATE COMPOUNDS**—This phase diagram describes two components (1 and 2) that are completely soluble in the liquid phase and completely insoluble in the solid phase. The system is solid below the straight line $aEb$; it is liquid above the curve $T_1ET_2$. In the area $T_1Ea$, equilibrium exists between crystals of component 1 and the liquid. In area $T_2Eb$ crystals of component 2 are in equilibrium with the liquid. $T_E$ is the temperature at the eutectic point.



**SYSTEMS WITH INTERMEDIATE COMPOUNDS**—Consider the case of two components that are insoluble in the solid phase and form an intermediate compound C that melts without decomposing. This phase diagram consists of the sum of two diagrams of the previous type (see Illustration 1).

2




tion of impurities to a pure substance always causes a lowering of the melting point. This is clearly demonstrated by the two curves $T_1E$ and $T_2E$.

Many binary systems are characterized by phase diagrams of the type shown in Illustration 1. Some of these systems, consisting either of two metals, two inorganic salts, or two organic substances, are listed in the table together with the corresponding eutectic temperatures (the melting points of the individual components are shown in parentheses). The eutectic temperature, mentioned previously, is the lowest temperature at which the liquid phase can exist.

Finally, the system is invariant at point $E$ because three phases are in equilibrium (solid 1, solid 2, and liquid):

$$v = 3 - \phi = 3 - 3 = 0. \quad (2)$$

The system is monovariant along the curves $T_1E$ and $T_2E$ where two phases are in equilibrium (solid 1 or solid 2, and liquid):

$$v = 3 - \phi = 3 - 2 = 1. \quad (3)$$

In the other areas there are no phases in equilibrium the system is bivariant.

*Systems with intermediate compounds.*—If the components 1 and 2 form a compound C, the phase diagram will assume different forms depending on whether the compound melts without decomposing or decomposes before it melts.

An example of this case is shown in Illustration 2. Here the components 1 and 2 form a compound C that melts at a temperature without decomposing.

The diagram in this case is easily interpreted if it is considered a combination of two simple phase diagrams such as the one shown in Illustration 1. The first of these shows substance 1 and the compound C as its components. The corresponding eutectic is formed at $E$. The second consists of substance 2 and the compound C and a eutectic at $E_2$. To see this clearly, first the right-

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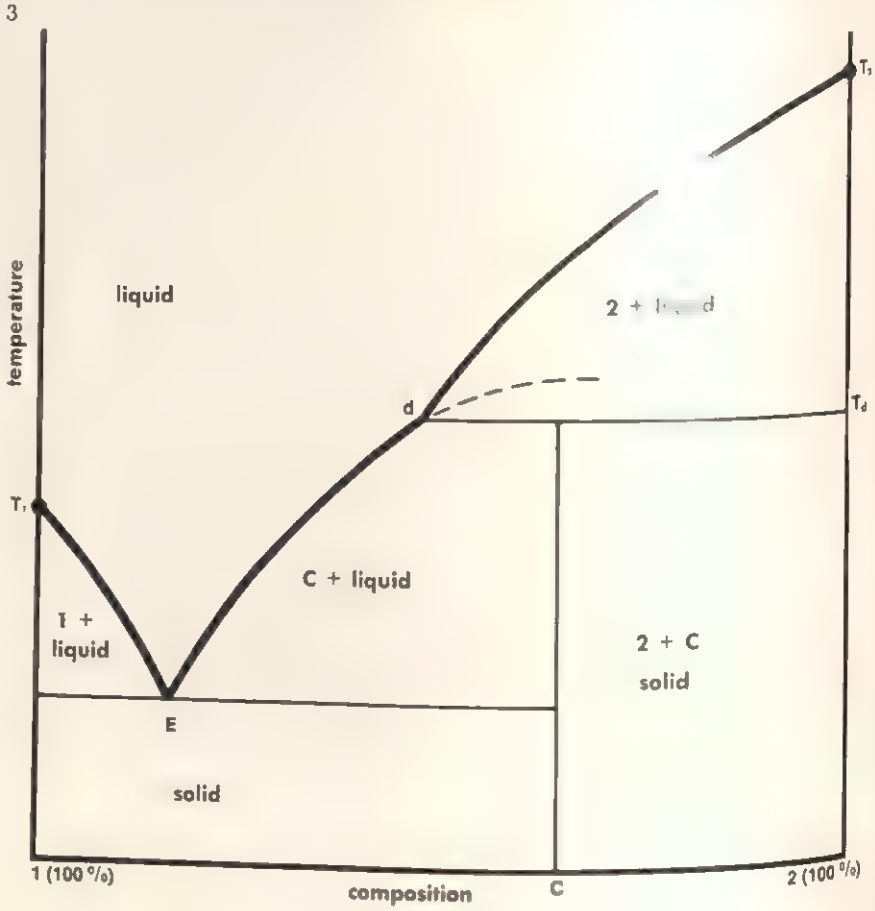



**PHASE DIAGRAM OF A SYSTEM WITH INTERMEDIATE COMPOUNDS THAT DECOMPOSE**—Components 1 and 2 form an intermediate compound that decomposes at a temperature $T_d$ before it reaches the melting temperature. The dashed curve shows what would happen if compound C did not decompose. The diagram shows the areas in which the various phases are stable.

SYSTEMS THAT FORM SIMPLE EUTECTICS

| System | | | | $T_E$ |
|---|---|---|---|---|
| gold | (1,064° C) | + | thallium | 131° C |
| lead | ( 326° C) | + | antimony | 246° C |
| aluminum | ( 657° C) | + | silicon | 578° C |
| cadmium | ( 321° C) | + | bismuth | 144° C |
| AgCl | ( 451° C) | + | KCl | 306° C |
| NaCl | 800° C) | + | $Na_2SO_4$ | 623° C |
| NaCl | 800° C) | + | CsCl | 493° C |
| LiF | 848° C) | + | NaF | 652° C |
| KF | 856° C) | + | NaF | 710° C |
| AgBr | 419° C) | + | KBr | 285° C |
| $CsNO_3$ | 413° C) | + | $Be(NO_3)_2$ | 310° C |
| aniline | −6° C) | + | $CH_3Cl$ | −71° C |

hand part of tl ram and then the left-hand part.

The phase dia shown in Illustration 3 is somew ore complex. The intermediate co d C does not melt in a stable form decomposes at a temperature $T_d$ it reaches its melting temperature dotted line shows what would have the nature of the curve if the comp C had not decomposed at tempera $T_d$. Up to this point, in fact, the graph vn in Illustration 3 is identical to th in Illustration 2. The area $T_2dT_d$ sents equilibrium between the com t 2 and the liquid. The pure compo 2 separates along the curve $T_2d$. the straight line $dT_d$, on the other reaction between the solid that ha rated and the liquid forms the nd C. This compound then dis the usual stability ranges in a man alogous to the example shown in tion 2.

## PHASE DIAGRAMS WITH THE COMPONENTS WHOLLY SOLUBLE IN THE SOLID PHASE

These phase diagrams are shown in Illustration 4. A two-component system that forms a continuous series of solid solutions is shown in Illustration 4a. Curve $T_1aT_2$ is the liquid curve, while curve $T_1bT_2$ is the solid curve.

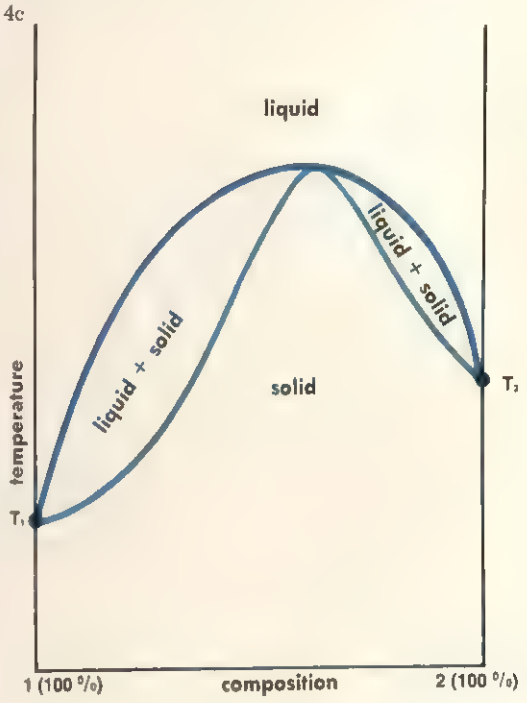
In the oval-shaped area $T_1aT_2bT_1$ equilibrium exists between the liquid and the separated solid solutions. The situation in Illustration 4a occurs quite frequently. It represents such alloys as platinum-gold, silver-gold, and cobalt-nickel.

Illustration 4b, on the other hand, shows a situation analogous to the previous one, except that it displays a minimum point. Alloys of manganese and copper, gold and copper, and silver and antimony are examples of systems that behave in this manner. The phase diagram in Illustration 4b is simply two diagrams of the 4a type joined together at the minimum point.

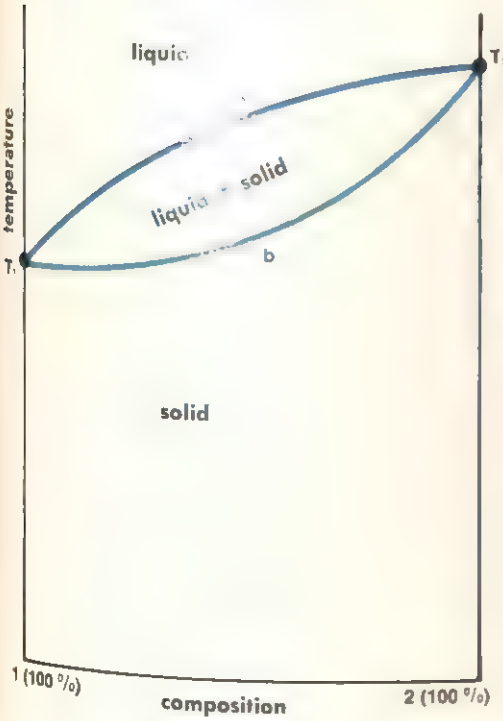
Finally, Illustration 4c shows a phase diagram that displays a maximum point. This is less common and is sometimes found in binary mixtures of certain organic substances.

In both Illustrations 4b and 4c there is a point where the solid curve and the liquid curve meet (the minimum point or the maximum point). At this point both the liquid and the solid have the same composition. There is therefore an abrupt transition from one state to the other.

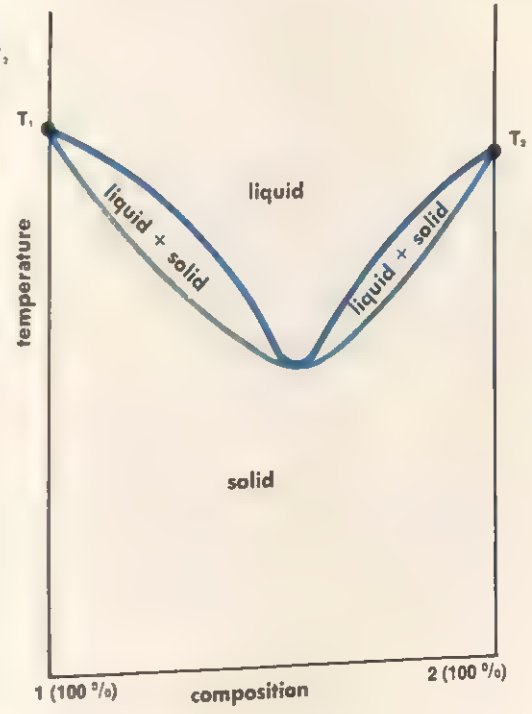
4c




4a




4b




**COMPLETELY MISCIBLE COMPONENTS** — In this case the components are completely soluble both in the liquid phase and in the solid phase. The formation of a continuous series of solid solutions is shown in Illustration 4a. Illustrations 4b and 4c, on the other hand, show either a minimum or a maximum point where there is an abrupt change from the liquid state to the solid state. The blue curves are the liquid curves; the green ones are the solid curves. Between these curves equilibrium between the liquid and the solid solutions exists; above the curves the system is wholly liquid, while it is entirely solid below.

# THREE-COMPONENT SYSTEMS | graphical representations

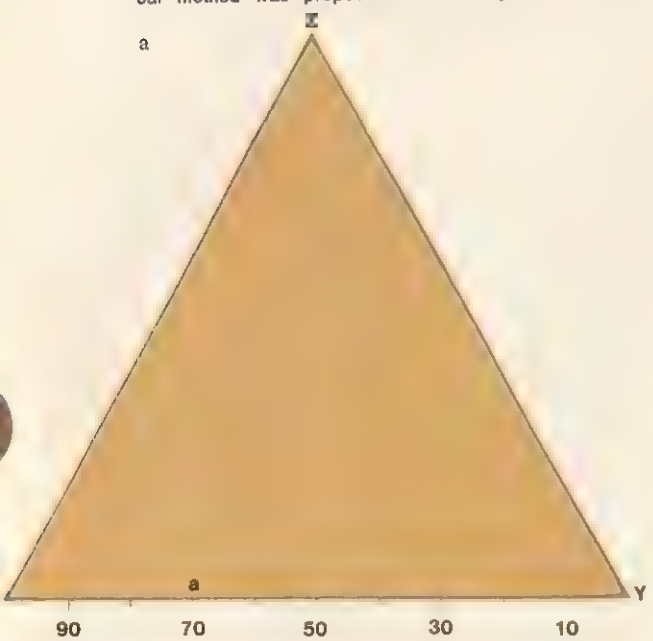
Single component systems and two-component systems have been discussed in previous articles. This article, therefore, is devoted to systems that consist of three components. These systems, often of great practical interest, are generally rather complex because, along with variable composition, pressure and temperature must also be considered.

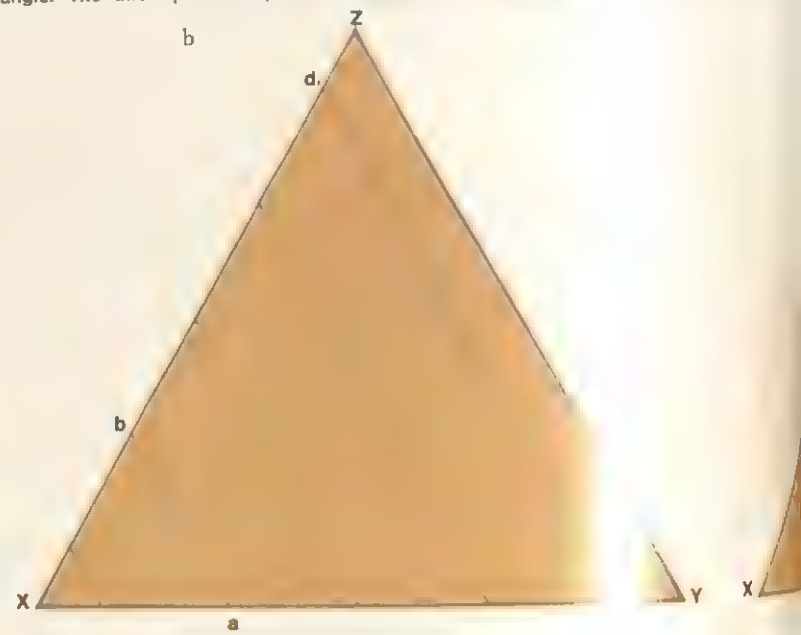
When the three components are liquids or solids, it is customary to simplify graphical representation of the system by considering only the condensed phases (liquid or solid) at constant pressure and at a selected temperature. The equilibrium conditions are thus studied in terms of how they vary with the composition alone.

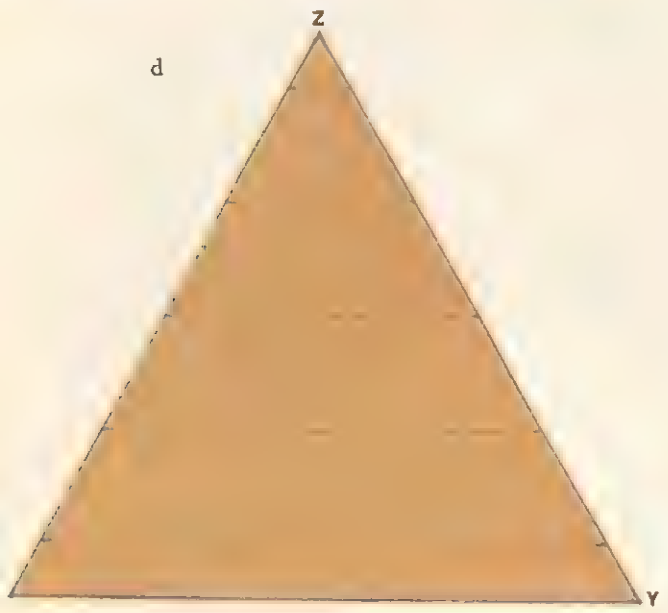
1

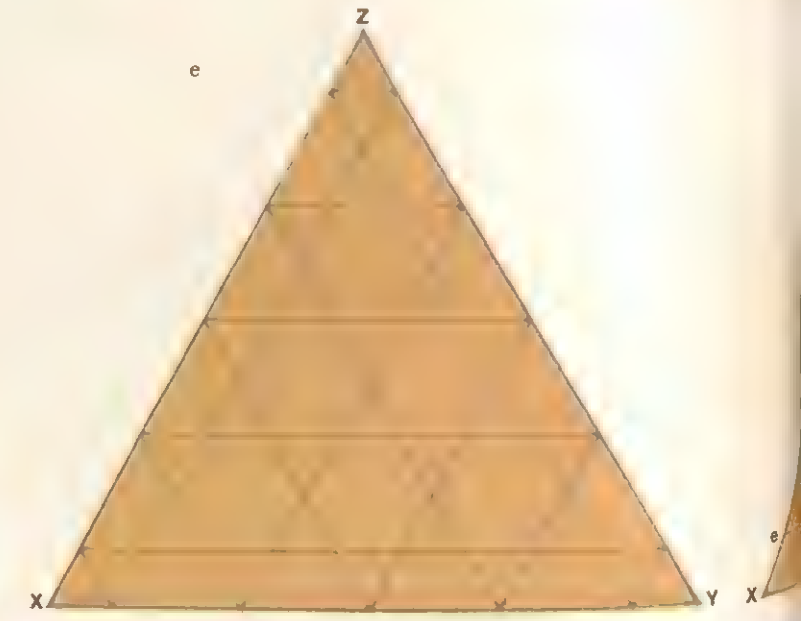
**THE COMPOSITION OF A TERNARY SYSTEM**—The first problem is finding a way to represent the composition of a ternary system in the simplest and most logical manner. Consider the system shown—a system consisting of three substances *X*, *Y*, and *Z* (*X* could be water, $H_2O$, *Y* chloroform, $CHCl_3$, and *Z* acetic acid, $CH_3COOH$). The most widely used graphical method was proposed in 1876 by the American physicist J. W. Gibbs. In this method the composition of the ternary mixture is represented by a point inside an equilateral triangle. Each point inside the triangle represents one (and only one) composition. Also, for any given composition it is always possible to find a point within the triangle that represents that composition. Illustration 1a is such an equilateral triangle. The three pure components *X*, *Y*, and *Z* are placed at the vertices. The three sides *XY*, *YZ*, and *ZX* of the triangle, therefore, represent the corresponding binary mixtures of the three substances. Taking the length of each side to represent 100, any point on a side thus represents a unique composition of the corresponding binary mixture.

For example, point *a* represents a binary mixture of the components *X* and *Y* having the



The principles [illegible] phase equilibria find application in p[illegible]al problems of metallurgy, in the [illegible]ics and glass industries, in the ge[illegible]al interpretation of minerals, in th[illegible]ly and utilization of salt deposits, a[illegible] many problems of physical and chemical separations such as distillation, crystallization, and extraction. The metallographic structure of an alloy can be understood completely only with the aid of an equilibrium diagram pertaining to the system.

following compos[illegible] n terms of mole percent):

$X =$ [illegible] (point a)
$Y =$ [illegible]

Vertex $X$ represe[illegible] $X$, vertex $Y$ therefore represents pure [illegible] on.

Now draw a la[illegible]nber of straight lines parallel to the si[illegible]site the vertex $X$, as shown in Illustration 1b. This establishes that any mixture containing 70 percent $X$ must always be represented by a point on the line segment $ab$. This, of course, is independent of the concentration and the quality of the remaining substances.

For example, a mixture containing 35 parts $X$, 10 parts $Y$, and 5 parts $Z$ (2) would always be found on the line segment $ab$ because the ratio

$$\frac{\text{concentration of } X}{\text{conc. } X + \text{conc. } Y + \text{conc. } Z} = \frac{35}{50} = \frac{70}{100} = 0.70.$$

The same reasoning can be applied to every line parallel to the side $ZY$. For example, the segment $c_1d_1$ represents all the mixtures that contain only 10 percent $X$, and so forth.

The same method can be used to express the concentrations of $Y$. Simply construct parallels to the side $XZ$ (Illustration 1c). For expressing the concentrations of $Z$, construct parallels to the side $XY$ (Illustration 1d). If Illustrations 1b, 1c, and 1d are combined, the result is the diagram shown in Illustration 1e. Now, given a mixture of any composition whatsoever, the point that represents it in the diagram is identified by determining the intercepts on the line segments parallel to $ZY$, $XZ$, and $XY$. For example, if it is desired to represent the mixture (2) above by means of a point, first it is necessary to write down the percent composition of the individual components;

$$X = 70\%; \quad Y = 20\%; \quad Z = 10\%.$$

Having done this, note in Illustration 1f that the point representing this mixture must simultaneously fall on the line segment $ab$ of the mixtures that contain 70 percent $X$, on the line segment $cd$ of the mixtures that contain 20 percent $Y$, and on the line segment $ef$ of the mixtures that contain 10 percent $Z$. This point is $P$. Conversely, it is just as easy to calculate that the mixtures represented by point $Q$ must have the following composition:

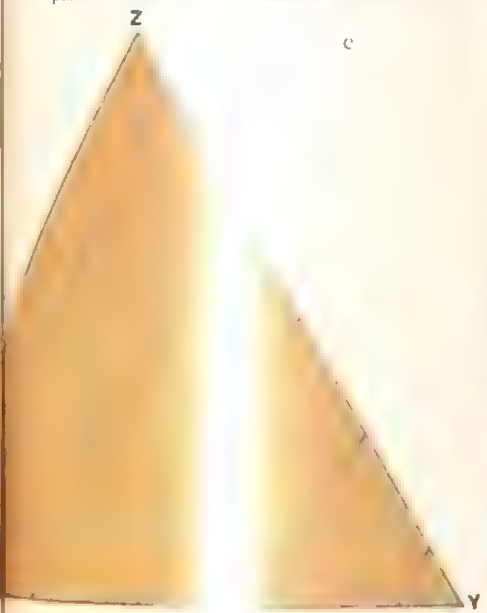
$$X = 30\%; \quad Y = 30.5\%; \quad Z = 39.5\%.$$

A number of characteristics make this graphical method particularly useful. For example, the sum of the segments $Pc$, $Pf$, and $Pb$ equals 100 parts.

$$Pc + Pf + Pb = \text{one side of the triangle} = 100 \text{ parts.}$$

The lengths of the individual segments, therefore, represent the percent composition of the three components of the mixture. To be more exact, each segment represents the composition of the component located at the vertex opposite the side touched by the segment.

Thus, the segment $Pf$ represents the percent of $X$, the segment $Pc$ represents the percent of $Z$, and finally, the segment $Pb$ represents the percent of $Y$ in the mixture.



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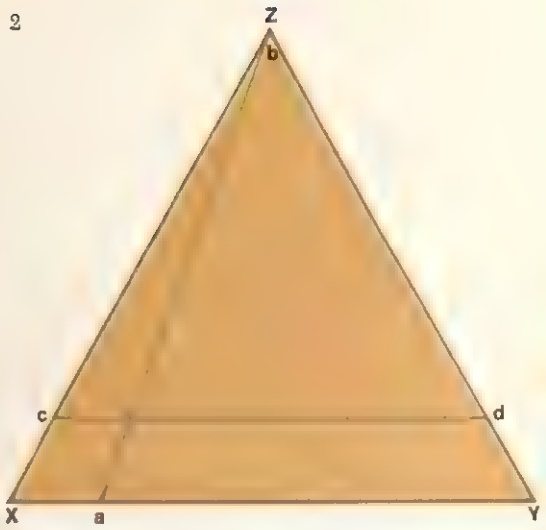
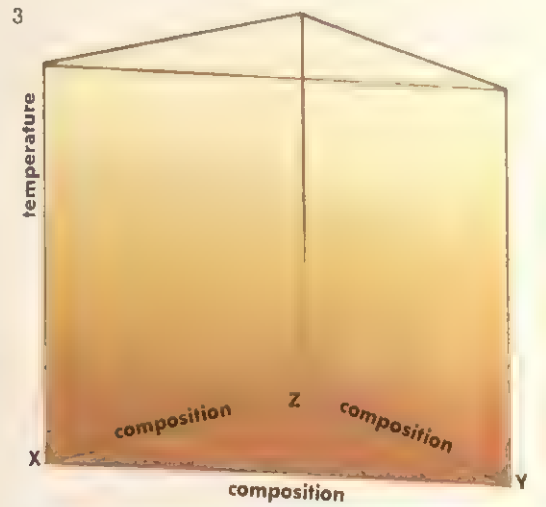



**TWO PROPERTIES BY MEANS OF EQUILATERAL TRIANGLES**—A second characteristic of the graphical scheme proposed by Gibbs refers to the mixtures represented by a line segment that starts at one of the vertices and ends on the opposite side; for example, the segment $ab$ shown in this illustration. The ratio of the concentrations of $X$ and $Y$ is constant for all of the mixtures represented by this segment:

$$\frac{\text{concentration of } X}{\text{concentration of } Y} = 4. \ldots$$

In other words, these mixtures will always contain four parts plus a fraction of a part of $X$ and one part of $Y$. Another characteristic that derives from the diagram is as follows. The concentration of the component found at any given vertex will always remain constant along segments parallel to the opposite side. For example, 18 percent of substance $Z$ is always present in the mixtures located along segment $cd$ of the diagram.

3




**THREE-DIMENSIONAL PHASE DIAGRAMS**—When systems at constant pressure are studied, the phase diagrams are usually drawn in three dimensions. This is done by means of a solid whose base consists of the equilateral composition triangle just described, but whose height represents the temperature variable.

To study processes at constant temperature, the solid is sectioned by cutting it along the horizontal plane corresponding to the temperature selected. The composition triangles obtained in this manner are called isothermal triangles.

# VAPOR PRESSURES | the laws that govern evaporation

Every liquid tends to evaporate to some extent. If a given quantity of liquid is placed in a closed vessel containing a vacuum above the liquid, a portion of the liquid evaporates until a certain pressure is developed; at that point the tendency toward evaporation is counteracted and balanced. This balancing phenomenon does not occur if the liquid is placed in an open container; instead, the evaporation continues until the liquid is gone. Everyday experience shows that the tendency of a liquid to evaporate is more pronounced as the temperature increases and, consequently, that the evaporation can be accelerated by heating the liquid.

This article deals with the laws governing the evaporation phenomena of pure liquids, particularly the laws that establish a relationship between the vapor pressure of liquids and the temperature of their systems.

## MICROSCOPIC ASPECTS OF THE PHENOMENON OF EVAPORATION

From a microscopic point of view, a liquid can be considered as an assembly of very small particles (normally molecules). Although these particles are in continuous and random movement, they are partially bound to each other by attracting forces. The temperature of the system is a macroscopic expression of these microscopic motions. The greater the average speed of the particles, the greater the temperature of the system.

Some of the moving particles occasionally pass through the surface of the liquid and enter the space above that surface, losing their bond with the other particles. As the temperature of the liquid is increased, this tendency to enter the space above increases correspondingly; the increased temperature increases the molecular agitation and, therefore, the average speed of the particles. This phenomenon is shown graphically in Illustration I. If the space above the liquid is a closed one, the phenomenon of evaporation causes particles to accumulate in the gaseous phase. However, the motion of particles in the gas also causes them to collide with the surface of the liquid. Some of these particles are recaptured and bonded again with the other liquid particles. This is the phenomenon of condensation—the opposite of evaporation. At a certain temperature, a state of equilibrium is attained—that is, as many particles abandon the liquid as are recaptured by it. Under a c lition of equilibrium, the pressure ex by the vapor above the liquid is c the saturated vapor pressure of th uid—or, more simply, the vapor pre

An increase in tem ure (or, molecular action) increa e vapor pressure of liquids. If th perature continues to increase, a is eventually reached where the at e forces that keep the particles u in the liquid state are no longer nt to balance the molecular agitati e liquid state then collapses and t por state becomes the stable on

## LAWS GOVERNIN EVAPORATION

Examination of the scopic picture clearly emphasizes th that tempera- ture and pressure a two physical factors that must b sidered in the study of evaporatio consideration of pressure, howeve d not be confined to the pressur loped by evaporation of the liq one. Artificial pressure can be exe the liquid by using any convenie thereby enabling an experim vary the parameter of pressur

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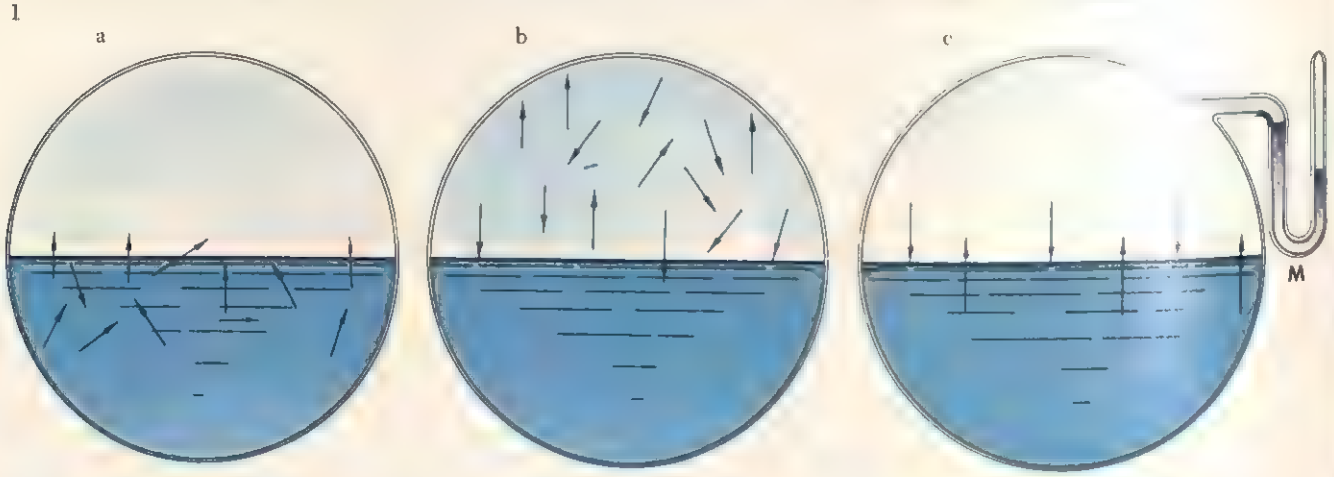


**A LIQUID IN A CLOSED VESSEL IN WHICH THERE IS A VACUUM IN THE UPPER PART** —In Illustrations 1a and 1b, the liquid and vapor states of a given substance are represented. The individual molecules—or particles—are represented at a particular instant of their random motion. When equilibrium is reached (Illustration 1c), the number of molecules evaporating is equal to the number condensing. The pressure read on the manometer M is the vapor pressure.

In the case of vaporation in the open air—as contraste[d] with evaporation in an enclosed contai[ner] the liquid is subject to the constant ssure of the atmosphere. Evapo[ration] in the open acts against this pre[ssure]. If the temperature of a liquid is b[rought] to the point where the vapor press[ure] reaches a value of one atmosphere, th[e] nomenon of boiling occurs; this ph[e]non is marked by the tumultuous [change] from the liquid state to the ga[seous] tate and is characterized by a fix[ed] perature called the "normal" boilin[g] t of the liquid.

Between the erature $T$ (always expressed in d[egrees] absolute, °K) and the pressure $P$ system, the following relationship rally exists:

$$\log P \quad \frac{H_e}{58\,T} + a. \qquad (1)$$

This is known a[s the] Clapeyron-Clausius equation (afte[r] French physicist B. P. E. Clapeyr[on] d the German physicist Rudolf Cl[ausius]. It is an approximate form of th[e] re rigorous equation developed by [Clausius] vron alone. In the Clapeyron-Cla[usius] quation $\log P$ is the logarithm [to] he base ten of the pressure; $\Delta H_e$ molecular heat of evaporation of liquid—the quantity of heat, in calo[ries] ceded to evaporate one mole of th[e] id; and $a$ is a constant.

If equation is applied twice to the same liqui[d] first time when the pressure and th[e] mperature are $P_1$ and $T_1$, the second when pressure and temperature ar[e] nd $T_2$, the following equations are o[b]tained:

$$\log P_1 = -\frac{\Delta H_e}{4.58\,T_1} + a \qquad (2)$$

$$\log P_2 = -\frac{\Delta H_e}{4.58\,T_2} + a. \qquad (3)$$

If equation (3) is subtracted from equation (2), the result is as shown in equation (4) below:

$$\log P_1 - \log P_2 = \log \frac{P_1}{P_2} = -\frac{\Delta H_e}{4.58}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \qquad (4)$$

If the value of $\Delta H_e$ is known, equation (4) can be used to calculate any one of the four parameters $T_1$, $T_2$, $P_1$, and $P_2$ when the other three are known. Assume, for instance, the following problem:

2

$$\log P_1 - \log P_2 = \log \frac{P_1}{P_2} = -\frac{\Delta H_e}{4.58}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{(a)}$$

$$\log 17.5 - \log x = -\frac{10{,}450}{4.58}\left(\frac{1}{293} - \frac{1}{323}\right) = -\frac{10{,}450 \cdot 30}{4.58 \cdot 293 \cdot 323} \qquad \text{(b)}$$

$$\log x = \log 17.5 + \frac{10{,}450 \cdot 30}{4.58 \cdot 293 \cdot 323} = 1.243 + 0.723 = 1.966 \qquad \text{(c)}$$

$$x = 92.5 \text{ mm Hg}$$

**THE VAPOR PRESSURE OF WATER AT 50° C**—The problem is to calculate the vapor pressure of water at 50° C (122° F), knowing that the vapor pressure of water amounts to 17.5 mm (0.68 in.) of mercury at 20° C (68° F), and that the latent heat of water evaporation has an average value of 10,450 cal/mole in the range from 20 to 50° C (68 to 122° F).

The problem is solved by means of equation (a). Using **x** to represent the value of $P_2$—and noting that $P_1 = 17.5$; 50° C = 323° K = $T_2$; 20° C = 293° K = $T_1$; and $\Delta H_e = 10{,}450$—substitute these values in equation (a) and obtain equation (b). Calculation of the value of the unknown gives the vapor pressure of water at 50° C (122° F).

knowing that the vapor pressure of water is 17.5 mm (0.68 in.) of mercury at 20° C (68° F or 293° K), calculate the value of the vapor pressure of water at 50° C (122° F or 323° K). Also known is that the value of $\Delta H_e$ for water in this range of temperatures amounts on the average to 10,450 cal per mole. Illustration 2 shows how this problem is solved. $P_2$ is found to amount to 92.5 mm (3.6 in.) of mercury.

A graphic solution of the same problem can be obtained. Equation (1) is the equation of a straight line; if $\log P$ is plotted against $1/T$ (as shown in Illustration 3), no more is left to do than to read the value of $\log P$ that corresponds to the inverse of the absolute temperature ($1/323 = 0.00309$), finding that $\log P = 1.966$. From this, the problem is solved: $P = 92.5$.

Other interesting problems can be solved by means of equation (4). For example, knowing that the boiling point of water is $T_1$ at pressure $P_1$, what will be the boiling point of water when the pressure becomes $P_2$? A problem of this type is solved in Illustration 4—for benzene instead of water.

If equations (1) and (4) are to be used, the value of $\Delta H_e$ in the temperature range concerned generally needs to be known. To study the variations of the boiling point of a liquid with variations of pressure (a problem of considerable technological interest), use can be made of an empirical rule first formulated by the English physicist Frederick T. Trouton. According to this rule, most simple, nonassociated liquids—those having a molecular weight of the order of 100—have a constant ratio between the value of $\Delta H_e$ at the boiling point and the boiling temperature $T_e$ (expressed in °K); this ratio is equal to approximately 21 cal per degree-mole. This rule is expressed as equation (5).

$$\Delta H_e / T_e \simeq 21 \qquad (5)$$

Using this equation, an approximate

**GRAPHIC SOLUTION**—This illustration is a graphic representation of the Clapeyron-Clausius equation for water in the temperature range from 20 to 50° C (68 to 122° F). The graph shows that the value of log **P** corresponding to 1/T = 0.00309 (T = 323° K, or 50° C) is 1.966. This means that $P_2 = 92.5$ mm (3.6 in.) of mercury. The result is thus identical to that obtained by equation (a) of Illustration 2.

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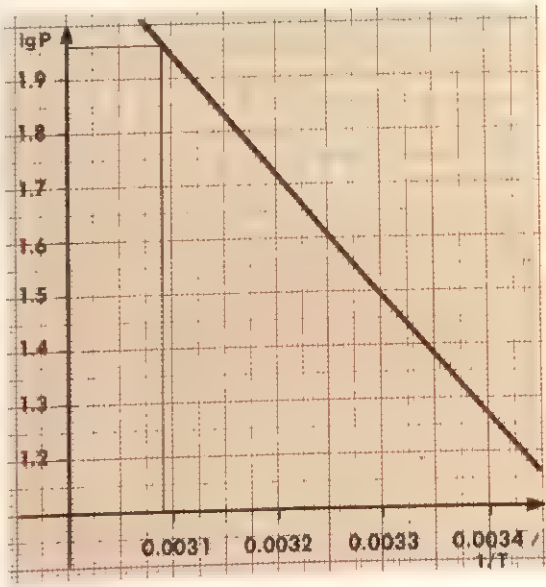

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$$\log P_1 - \log P_2 = \log \frac{P_1}{P_2} = -\frac{\Delta H_e}{4.58}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (a)$$

$$\log \frac{1}{2} = -\frac{7{,}500}{4.58}\left(\frac{1}{353} - \frac{1}{x}\right) \quad (b)$$

$$\log \frac{1}{2} = -0.301 \quad (c)$$

$$0.301 \cdot \frac{4.58}{7{,}500} = \frac{1}{353} - \frac{1}{x} \quad (d)$$

$$\frac{1}{x} = \frac{1}{353} - \frac{0.301 \cdot 4.58}{7{,}500} = \frac{7{,}500 - 0.301 \cdot 4.58 \cdot 353}{353 \cdot 7{,}500} \quad (e)$$

$$x = \frac{7{,}500 \cdot 353}{7{,}500 - 0.301 \cdot 4.58 \cdot 353} = 377° \text{ K} \quad (f)$$

$$377° \text{ K} = 104° \text{ C} = 219.2° \text{ F} \quad (g)$$

**THE BOILING POINT OF BENZENE AT A PRESSURE OF 2 ATMOSPHERES**—Knowing that benzene boils at 80° C (176° F) at a pressure of 1 atmosphere, and that the latent heat of boiling $\Delta H_e$ is equal to 7,500 cal/mole, determine the boiling point of benzene at a pressure of 2 atmospheres.

The problem is solved by means of equation (a). Letting x represent the value of $T_2$—and noting that $P_1 = 1$ atmosphere; $T_1 = 80°$ C (353° K); $P_2 = 2$ atmospheres; and $\Delta H_e = 7{,}500$ cal/mole—equation (b) is obtained. Solving this equation obtains the value of x, which is equal to 104° C (219.2° F or 377° K). The boiling point of benzene at 2 atmospheres is found to be 24° C (43.2° F) above the normal boiling point.

value of $\Delta H_e$ can be obtained by multiplying $T_e$ by 21, as shown in equation (6).

$$\Delta H_e \simeq T_e 21 \text{ (cal/mole)} \quad (6)$$

In the problem presented in Illustration 4, for example, if the value of $\Delta H_e$ is unknown, equation (6) can be used to calculate the value of $\Delta H_e$, giving $\Delta H_e = 353 \times 21 = 7{,}413$. This compares with a precise value of 7,500 cal/mole, an excellent agreement for an approximate value.

An even more approximate rule that is often useful for technical purposes was formulated by the American chemist J. M. Crafts for expressing the dependence of the boiling point on the pressure. According to this rule, the increase in the boiling temperature $\Delta T$ that is associated with a pressure increase $\Delta P$ (expressed in atmospheres) is given by the expression shown in equation (7),

$$\Delta T = 0.091\, T_e \Delta P, \quad (7)$$

where $T_e$ is the boiling point of the liquid (in °K).

Applying equation (7) to the problem shown in Illustration 4,

$$\Delta T = 0.091 \cdot 353\,(2-1) = 32° \text{ C}. \quad (8)$$

This compares with a correct value of 24° C (43.2° F). The expression of equation (7) is a rather approximate one; in general, however, the smaller the values of $\Delta P$ the more satisfactory are the values provided by this expression.

For example, if the problem shown in Illustration 4 had been one of finding the boiling point of benzene when the pressure changes from 1.0 to 1.5 atmospheres, a calculation based on equation (4) and carried out in a manner analogous to that shown in Illustration 4 would have led to the solution $\Delta T = 14°$ C. Using equation (7), however, would produce the following:

$$\Delta T = 0.091 \cdot 353 \cdot 0.5 = 16° \text{ C}. \quad (9)$$

There is much better agreement in this case than was obtained in the calculation conducted in equation (8).

## MEASURING VAPOR PRESSURES

The most direct and accurate methods for the measurement of vapor pressures are: (1) the dynamic method, in which a liquid is boiled in a vertical tube in a thermometer (shielded against radiation) placed in the condensing vapor and the pressure transmitted to a pressure gauge by means of a gas of smaller molecular weight than that of the vapor; and (2) the static method in which the coexistent liquid and vapor are enclosed in a bomb maintained at a constant temperature $T$ and the pressure transmitted to a pressure gauge through a capillary opening containing the vapor phase if $T$ is below room temperature, or the liquid phase (or an inert liquid, such as mercury) if $T$ is above room temperature. The static method is also applicable to the measurement of the sublimation pressures of solids. Exceedingly small vapor pressures are determined by measuring the rate of effusion of the vapor through a small hole and applying the effusion equation of kinetic theory. Difficulties in measuring low temperatures led the International Committee on Weights and Measures in 1958 to propose as the international standard of thermometry a scale from 1° to 5.2° K (about −458° to −450° F) based on the vapor pressure of liquid He[4].

## PRACTICAL APPLICATIONS

The Haber process for the chemical utilization of the inert nitrogen of the air furnishes a striking illustration of the importance of vapor pressure. The reaction $N_2 + 3H_2 = 2NH_3$ does not take place at all when nitrogen and hydrogen are brought together under ordinary conditions, whereas ammonia is easily decomposed on moderate heating. The principles of equilibrium teach that the equilibrium would be displaced in favor of ammonia by increasing pressure and lowering temperature. Using a catalyst made mostly from iron and employing moderately high temperatures and extremely high pressure, the German chemist Fritz Haber caused nitrogen from the air to combine with hydrogen in the ratio of one atom to three, producing ammonia.

A typical ammonia synthesis converter for operation in the high-pressure range, at about 1,000 atmospheres, is a thick-walled carbon steel vessel that produces from 250 to 400 lbs of ammonia per hour per cubic foot of catalyst.

The process for synthesizing methanol is in general similar to that for ammonia. Typical operating conditions are 200 atmospheres of pressure. At pressures from 200 to 1,000 atmospheres, higher alcohols are formed.

# DRY CHEMICAL ANALYSIS | using flames and colors to identify chemical substances

Inorganic compo[illegible] are familiar household items to alm[illegible] everyone; table salt (sodium chloride[illegible] alk (calcium sulfate), sodium bi[illegible] ate, and boric acid are examples of [illegible] compounds common in everyday [illegible] Many other inorganic compound[illegible] s common in the household; they [illegible] numerous that they are classified [illegible] tegories as salts, acids, alkalis, anh[illegible] and oxides, according to their [illegible] es and the reactions that they p[illegible]

The category [illegible] h an inorganic compound belon[illegible] termined by analysis. Inorganic [illegible] ive chemical analysis seeks to [illegible] what elements make up the class of substances called inorganic compounds, which are classified as minerals and which are widely distributed in nature.

## COLOR: A FIRST AND USEFUL INDICATION

Sometimes color can be used as a clue to the identity of a substance or at least some of its components. Copper salts have a blue or bluish-green coloring that is retained even in solution. Cobalt salts crystallized with water (hydrates) are pink, and those crystallized without water are blue. Both of them, when dissolved in

1a

**COLOR**—Sometimes [illegible] stance can be recognized simply by it[illegible] These illustrations show a series of s[illegible] of which are intensely colored and [illegible] distinguished from one another. In the [illegible] ound of illustration 1a are crystals of co[illegible] fate, with the characteristic blue colo[illegible] they retain even in solution. The solut[illegible] potassium dichromate shown in illustration 1b preserves the brilliant orange color of its solid state. In illustration 1c, both the hydrated cobalt salt (in this case, the chloride) and the solution containing it are a deep rose color; the color is characteristic of a complex ion in which the cobalt is surrounded by six molecules of water. The complex is a positive bivalent one.

1b

1c

**SUBLIMATES**—To distinguish between white substances without performing tests on them is impossible. A simple test consists of placing a small amount of the substance at the bottom of a test tube and heating it over a Bunsen burner. The substance melts, and a film of powder (sublimate) is gradually deposited on the cold walls of the test tube. This indicates that the substance is volatile. Useful information regarding the compound can be derived from the color of the sublimate. For example, a white sublimate of arsenic trioxide ($As_2O_3$)

2a

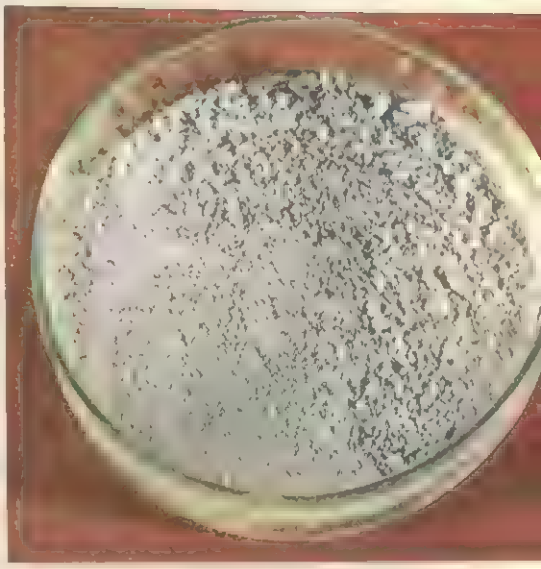
2b

is shown in Illustration 2a; a bright yellow sublimate of arsenic trisulfide ($As_2S_3$) is shown in Illustration 2b; and a dark black sublimate of mercury sulfide (HgS), in Illustration 2c.

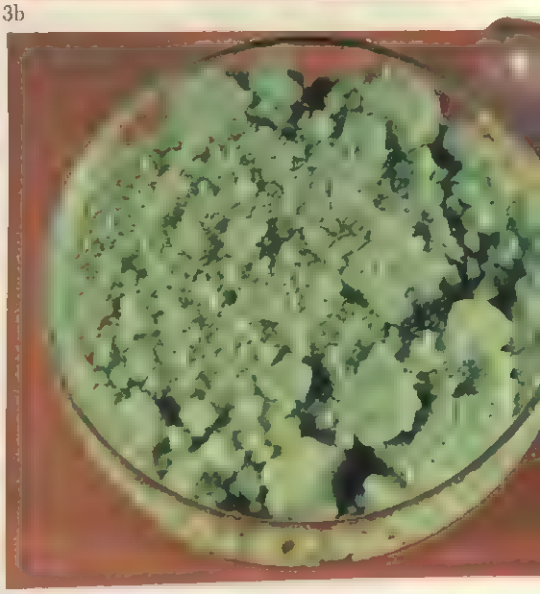
2c

water, give the solution a pink color. Many compounds containing chromium are yellow or orange, according to the oxidation states of the element (Illustration 1). However, not every compound can be identified by color because many substances, although extremely different in composition and characteristics, are white or are identical in color. Some white compounds such as those of arsenic and lead are highly poisonous, but have an appearance similar to that of common table salt, sugar, or sodium bicarbonate. These observations are valid if the compounds are present singly, but identification is difficult if compounds are mixed. (For example, when a light-colored compound is mixed with a dark-colored one, the presence of the former is difficult to detect.) Identification of compounds that

3a



3b



3c

3d

**DEHYDRATION**—Dehydration takes place when a hydrated substance is heated. The heat causes the compound to lose its water of crystallization and, sometimes, its color. The bluish-green hydrate of copper sulfate becomes white (Illustration 3a). The hydrate of nickel chloride (Illustration 3b) becomes yellow (Illustration 3c). Cobalt chloride changes from deep pink to blue (Illustration 3d).

are dissolved in water is more difficult yet. In most cases the compound or mixture of compounds must be analyzed; that is, it must be subjected to the action of certain substances (reagents) so that the reactions that take place or the modifications that the compounds or reagents undergo may be observed. On the basis of such observations, the nature of the compounds can be determined.

4

**VAPORS** — One phenomenon caused by the simple heating of certain substances is the formation of vapors as a result of internal reactions. This illustration shows abundant purple-colored vapors of iodine arising from a heated mixture of iodides and oxidizing substances.

## TEST IN AN OPEN TEST TUBE

A small quantity of material may be placed in a simple glass test tube. The test tube is held over a flame so as to subject the material to the action of heat. If the upper part of the test tube becomes covered with a powdery film (sublimates), the presence of substances that volatilize and do not melt (that is, substances that can be sublimated) is indicated. Examples include arsenic trioxide ($As_2O_3$), mercurous chloride ($Hg_2Cl_2$), and mercuric chloride ($HgCl_2$), if the sublimate is white; sulfur or arsenic trisulfide ($As_2S_3$), if the sublimate is yellow; and mercury sulfide (HgS), if the sublimate is black (Illustration 2).

Other interesting observations can be made by heating inorganic compounds in the aforementioned manner. A pinkish-colored compound can be assumed to be a hydrated cobalt salt. A change in the color of the compound from pink to blue when heated in a test tube confirms the presence of a cobalt hydrate. When a cobalt hydrate is heated, it loses its water of crystallization and appears in its anhydrous form, which is blue (Illustration 3).

Copper and nickel salts are green, and a trained observer can easily distinguish one from the other. In case of doubt, heating the substance in a test tube can provide a good test. Copper salts change from bluish-green to white, and nickel salts become yellow because of the loss of the water of crystallization (Illustration 3).

The simple heating of substances provides further information. Sometimes colored vapors are given off by heated materials. Purple vapors are a sure indication of the presence of iodides and of oxidizing substances (such as manganese dioxide), or of chromates, which cause simple iodine to separate from the iodide and to pass into the state of purple vapor (Illustration 4). In a similar manner, bromides in the presence of oxidizing substances give off vapors of bromine, which are reddish; nitrogen tetroxide ($N_2O_4$), a gas that is given off by certain nitrates (such as lead nitrate) when they decompose under the action of heat, is also reddish.

Not all gases and vapors are colored, however. Although many of those that arise from the decomposition of certain substances are invisible, in some cases they can be recognized by a characteristic odor. The familiar suffocating odor of ammonia, a colorless gas, is readily noticeable when diammonium phosphate, $(NH_4)_2HPO_4$, or ammonium metaborate, $NH_4BO_2$, is heated in a test tube; these ammonium salts are obtained by the reaction of ammonia with phosphoric acid and boric acid, respectively. These salts, unstable when heated, tend to decompose into the two compounds of which they are composed; the volatile ammonia is given off, and the nonvolatile acid remains in the test tube.

When a sulfur match is lighted, it gives off a sharp odor of burned sulfur because of the sulfur dioxide ($SO_2$) that is formed by the combustion of the sulfur of the match in the oxygen of the air. The same odor is present when either calcium sulfite, $CaSO_3$, or silver sulfite, $Ag_2SO_3$, is heated, because sulfur dioxide is one of the products of decomposition.

## THE FLAME TEST

The flame test is an useful and interesting test, com performed in the course of tradition litative chemical analysis. This t quires a platinum wire 5 to 6 cm it 2 in.) long, fixed in a glass tub d of the platinum wire is dipp hydrochloric acid (HCl), and a l the substance to be examined (in fered form) is made to adhere to wire is then held in the nonlumi rt of the flame of a Bunsen burner ich the quantity of air that is m h the gas can be controlled by a v ereby regulating the luminosity a t of the flame. At this point in th he flame may take on an intense a tiful coloring. Sodium salts giv ne a brilliant yellow color, lithium carmine red, and copper salts an ld green. Calcium salts produc intermittent flashes of yellowish llustration 5).

With a little pra chemical analyst can use the fl t to recognize the presence of var tals in a substance. He can dist for example, those substances co g barium from those containing co (even though the green color that impart to the flame is very similar d he can differentiate substances ining lithium from those contain strontium, although both give similar red colors. (For more information on modern flame analysis, consult the following article.)

## INSTRUMENTAL METHODS OF DRY CHEMICAL ANALYSIS

In addition to the classical methods of dry chemical analysis, the modern chemist uses a number of new techniques that have been developed around optical and electronic instrumentation. These instruments serve to extend the chemist's normal senses of sight, hearing, smell, taste, and touch. They provide greater sensitivity in determining small quantities of chemical substances and greater accuracy in identifying and measuring the chemical components of materials. Because the number of instrumental methods is large and the principle of their operation is often quite complex, only a

few simple exam[illegible]s will be discussed.

One method o[illegible]dentifying and measuring the eleme[illegible]n a chemical sample is by use of an [illegible]rical discharge. Here the sample is u[illegible]s an electrode, similar to the wel[illegible]d in an arc welder. A very high-v[illegible]or high-current discharge is then [illegible]occur between the sample electro[illegible]d another electrode. As in the case [illegible]rc welder, a great deal of energy [illegible]ated by, and present in, the d[illegible] Just as the arc-welder energy [illegible]to melt two pieces of steel together, the arc discharge is used to decompose the dry chemical sample. The atoms liberated by the decomposition are then excited and emit light, which can be measured. Just as in the case of the flame, the color or wavelength of the emitted light can be used to identify the elements present in the sample, and the amount or intensity of the light can be used to determine how much of each element is present.

Another instrumental method of dry chemical analysis utilizes the reflection of light from a sample. Grass and leaves appear green because of the chemical compounds present in them. These compounds absorb light of all colors other than green so that the green colors are reflected rather than absorbed. In the same way, chemical compounds in an unknown sample reflect mostly the colors, or wavelengths of light, that are not absorbed. A beam of light can be directed onto the sample, and the intensity and color of the reflected light used to analyze the sample for its chemical constituents.

**FLAME TEST**—[illegible]inum wire and [illegible]stances heated [illegible]requires only a platinum wire and burner. Certain substances heated in the flame color the flame: sodium (Illustration 5a) gives a characteristic yellow color; calcium (Illustration 5b) gives off red flashes; copper (Illustration 5c) gives a brilliant emerald-green flame, with bright flashes; and barium (Illustration 5d) gives a persistent pale green flame.

5a 5b 5c

5d

# THE FLAME IN CHEMISTRY | a tool for analysis

1

**RADIATING ATOMS**—A simple flame, such as the one produced here by a Bunsen-type burner, is capable of generating rather high temperatures. The temperature of the illuminating gas-air flame here is approximately 1,800° C (3,272° F)—hot enough to heat a platinum wire to incandescence. Many free metal atoms heated to this temperature are excited and give off radiation (light) characteristic of the metal. In flame emission spectrometry, this radiation is used to measure the kind and concentration of metal species in a solution.

Since the dawn of time, fire and flames have fascinated [man], assisted, and at times been harmful to [man]. Although the first use of fire by [man] occurred long before recorded history, [it] has been ascertained that fire played [an] important role in the formation and [advancement] of civilized societies.

The power and importance of fire were well recognized [by] early societies attached a religious significance to the flame, while even in the relatively enlightened Middle Ages fire, along [with] earth, air, and water, was considered [to be] one of the four basic components of matter. Not until the seventeenth century was it recognized that fire was not the outward sign of an intensely hot gas. Later, fire was regarded as an extremely rapid combination of a substance with oxygen from the air. The combustion, or oxidation as it is called, is so rapid that an appreciable amount of light and heat are generated.

Although [even] this latter view of fire and flame [is] unnecessarily limited. Today, scientists recognize that a flame is no more and no less than a vigorous chemical reaction. The reaction generates heat and can excite species that are excited by the high temperature to produce light. Because [Lavoisier]'s definition is no longer restricted to the inclusion of oxygen, flames can be produced by combination of any species provided the reaction is sufficiently exothermic and liberates enough heat. As a limiting case, it may be pointed out that an explosion is a form of uncontrolled, rapidly propagating flame.

Because the nature of the flame is just that of a chemical reaction, it can be used as a medium for examining rapid reactions that would not occur in a less energetic medium. Many important chemical reactions, such as those employed in metallurgical industrial processes, were made possible by the flame. However, although it is used heavily in industry, perhaps the most common use of the flame in laboratory chemistry today is in the field of chemical analysis.

The basis for chemical analysis using the flame is found in the science of spectroscopy. In this field, chemical species are identified and measured according to the light they radiate when excited. Anyone who has seen a welder heat a copper wire or copper tubing has perhaps remarked on the beautiful green color produced. This green color is characteristic of the presence of copper. Also, the presence of table salt spilled on a gas stove burner or in a campfire can impart the

**BORAX BEADS**—One of the simplest flame tests used to determine the presence of certain metallic elements is the borax bead test. The bead is obtained as follows: First, a platinum wire bent into a loop is heated in an oxidizing flame. Then, while still red hot, the loop is dipped into sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), as shown in Illustration 2a. In the flame, the borax expands (Illustration 2b), liberating water of hydration. It then fuses into a colorless, transparent, glassy mass—the bead (Illustration 2c).

2a

2b

2c

3a

3b

3c

**COLORED BEADS** — In order to identify metallic elements in unknown compounds, the clear bead is again heated to incandescence and immediately dipped into the substance to be analyzed. Held in the flame and then cooled, the bead takes on a characteristic color. A purplish-red bead (Illustration 3a) indicates the presence of manganese in the unknown; a deep blue bead (Illustration 3b) indicates the presence of cobalt, while a pale blue bead (Illustration 3c) indicates traces of copper.

bright yellow color of sodium to the flame. Just as with copper or sodium, every other chemical element, because of the unique electronic configuration of its atoms, has its particular spectrum of colors and, the can be made to emit light or radia hat can be used in its identification ample of such a simple flame tes wn in Illustrations 2 and 3. Some colors and the wavelength of the itted light are shown in the accompan table. If the emitted radiation is in visible wavelength region—between 00 and 7,000 Å (Angstroms)—it is d light. If, however, the radiation either the ultraviolet (below 4,000 or infrared (beyond 7,500 Å) regi it is more properly called radiation. Because the spectral characteristics e elements are unique, the elements have often been employed for visual effect. The characteristic glow of a neon lamp and the brightly colored pyrotechnics of fireworks display are examples of this. In chemical analysis, however, the s are used to identify and measure concentration of elements in an wn sample. In most cases, the el is found in solution, along with ot pecies, whose identity and concentr may or may not be sought. Beca he free atoms in the flame produ characteristic colors, the solution be converted to free atoms. This lly done with a nebulizer, often ca n atomizer or simply a sprayer. Usi is device, the solution to be analyze sprayed into the flame. The high temperature of the flame then partially decomposes the sample in the solution to free atoms.

The light given off by the atoms in the flame can then be used to determine both the kinds of elements in the sample and the concentration of each. The wavelength or color of the light indicates which elements are present, while the intensity of the light at each wavelength gives information on the amount of each element. To determine the wavelengths and intensity of the light, a device called a spectrometer is often used. With this device, samples can be rapidly analyzed for any of as many as 40 metallic and nonmetallic elements. The entire technique of measuring the emitted light from the flame is called flame emission spectrometry.

4a 4b

**THIOSULFATE TEST**—Certain elements may be identified using sodium thiosulfate ($Na_2S_2O_3$). Sodium thiosulfate (Illustration 4a), when heated, decomposes into sodium sulfate, sulfur, and sodium sulfide (Illustration 4b). The sodium sulfide is the most important because it forms the corresponding metallic sulfide of the unknown and has a characteristic color. If antimony(III) oxide, $Sb_2O_3$, is made to react with sodium thiosulfate, a reddish-orange color results (Illustration 4c), while with arsenic(III) oxide, $As_2O_3$, a canary yellow color results (Illustration 4d).

4c 4d

Flame emission spectrometry is a widely used technique for elemental analysis. In particular, the technique is almost universally employed in the determination of electrolyte concentrations in blood and other biological fluids. Sodium, potassium, calcium, and magnesium are determined in these clinical analyses to such an extent that completely automated systems have been developed. Without any attention from a technician, these automated instruments can perform

Colors and Wavelengths for Flame Emission of Several Elements

| Element | Wavelength (Angstroms) | Color |
|---|---|---|
| sodium (Na) | 5,890 | yellow |
| calcium (Ca) | 4,227 | brick red |
| potassium (K) | 7,665 | red |
| magnesium (Mg) | 2,852 | ultraviolet |
| aluminum (Al) | 3,961 | violet-white |
| zinc (Zn) | 4,181 | many colors |
| silver (Ag) | 3,281 | ultraviolet |
| barium (Ba) | 5,535 | yellowish-green |
| strontium (Sr) | 4,607 | bright red |
| copper (Cu) | 3,247 | green |

a great number of analyses each hour at a level of precision difficult to achieve under direct operator control.

Another flame analysis technique associated with the flame emission procedure is called atomic absorption spectrometry, or AA as it is often abbreviated. In AA, the atoms produced in the flame are made to absorb light or radiation from an external light source rather than to emit, or give off light. This is possible because the changes in electronic energy states giving rise to the emitted light are two-way processes.

It follows, therefore, that atoms existing in the lower energy state in the flame can absorb light energy just as those in the higher electronic state are capable of liberating energy in the form of light.

Because atoms, like most physical systems, prefer to be in the lower energy state, most atoms in the flame are found in the lower state. The AA process, unlike flame emission, uses these lower energy atoms. Therefore, in some cases, AA is the most convenient technique to use, since it has more atoms with which to work.

This advantage, and others, has made atomic absorption spectrometry the most widely used technique for elemental analyses. The method came into prominence in the 1960s.

5a

5b

**FUSION WITH SODIUM CARBONATE**—Compounds of chromium and manganese often can be recognized by their characteristic colors. Chromium salts are usually yellow, while manganese salts may be purple, pink, green, or black, depending on the oxidation state of the element. Sometimes, however, these elements cannot be identified at first glance, or their presence may be in doubt. In these instances a simple test is used. The substance is melted with a mixture of sodium carbonate, $Na_2CO_3$, and potassium nitrate, $KNO_3$. The mixture of sodium carbonate and potassium nitrate is mixed with sodium chromate (illustration 5a), or with manganese(II) carbonate (illustration 5b). Illustration 5c shows the first mixture as it is melting and taking on a bright yellow color. In illustration 5d the second mixture is shown completely melted, with its typical deep green color.

5c 5d

# QUALITATIVE WET CHEMICAL ANALYSIS | principles and special techniques

Chemical an[illegible]ses of inorganic compounds in the [illegible] or solid state, as opposed to such [illegible]ompounds in solution, provide only [illegible]neral idea of the composition of the [illegible]stance being analyzed. Even though [illegible]an approach will identify some of the constituents of the unknown, it cannot be regarded as a complete analysis. Nor can it be said that analytic tests in the solid state are always reliable.

Accurate and reliable wet qualitative analyses of inorganic compounds are carried out in solution; that is, both the unknown substance and the appropriate reagents are in solution form. Such solutions are prepared by dissolving the substance in pure water or in another solvent. Under certain conditions, it is desirable to dissolve a given compound in an acidic, basic, or salt solution, or even in a nonaqueous solvent.

Salts in aqueous solution undergo electrolytic dissociation; that is, the ions of the crystal lattice separate into oppositely charged particles. The positively charged particles are called cations. These are generally metallic ions (atoms of metals that have lost one or more electrons). The negatively charged particles are called anions. These may be nonmetallic or metalloid ions, or negatively charged functional groups of atoms called radicals. Anions have a negative charge because the particle or radical contains more electrons than protons.

Cations and anions are the particles that react in inorganic solution chemistry. Such reactions are, therefore, called ionic reactions. Aqueous solutions of different salts of the same metal—for example, cobalt chloride, $CoCl_2$, cobalt sulfate, $CoSO_4$, and cobalt nitrate, $Co(NO_3)_2$—will all react positively to the test for the $Co^{2+}$ ion present in all three solutions. In this example, a characteristic reaction identifies the ion common to the three salts. It does not, however, reveal which salt is being analyzed. Other tests are required to identify the three different anions.

Consider a solution of several salts (the most common cause). Under these circumstances, several different cations and several different anions are dispersed throughout the solution. It is not possible to determine how these ions were combined in the original solid state, but it is possible to identify the ions one by one (with a few exceptions). In other words, qualitative analysis of the solution will yield the overall ionic composition of the mixture. In most practical cases, this is quite sufficient.

## IONIC REACTIONS

Qualitative wet chemical analyses make use of those ionic reactions that produce a visible change, although occasionally the odor of a gas is used to identify an ionic substance.

The chemist recognizes specific reaction products, and thus can identify the ion that yielded the product when it reacted with a given reagent. By identifying and eliminating ions one by one, the complete composition of the mixture can be determined. The reactions of qualitative analysis are generally of three types:

1. The formation of a precipitate having a characteristic color or appearance.
2. The production of a soluble substance that changes the color of the solution.
3. The production of a gas having a characteristic color or odor.

**COBALT SALT[illegible]** [illegible]utions of different salts of the same m[illegible] [illegible]ll all react positively to the test reactio[illegible] [illegible]e metallic ion. The metal In the illustratio[illegible] [illegible]balt. Its neutral solution is pink, and the [illegible]solution is sky blue. The watchglass in [illegible]eground contains solid cobalt chloride [illegible]is dark pink in color.

1

2

**CHARACTERISTIC REACTION** — Precipitation of a metal by means of a complex reagent is a typical reaction. Nickel, for example, when precipitated with dimethylglyoxime from an ammoniated solution, yields a red precipitate.

**CADMIUM SULFIDE**—Cadmium, like nickel, can be precipitated by means of hydrogen sulfide ($H_2S$). This reaction is used extensively for analytic purposes. The reaction produces a precipitate of cadmium sulfide. The characteristic yellow color of cadmium sulfide identifies the cadmium ion ($Cd^{2+}$) at once.

3

4a

**COLOR CHANGE AND GAS PRODUCTION**—The reaction of an acid solution of iron(III) salts with potassium ferrocyanide results in a dark "Prussian" blue solution (illustration 4a). In illustration 4b dense fumes of hydrogen chloride are produced from the reaction of sulfuric acid and sodium chloride.

4b

A single reaction is not always adequate, however, to recognize an ion. It sometimes happens that the product of a reaction does not provide full confirmation of that particular ion because the product is not specific for the ion. Put another way, several different ions may react with the same reagent to yield products that have the same physical characteristics.

For example, consider a solution of lead nitrate, $Pb(NO_3)_2$, another of silver nitrate, $AgNO_3$, and a third of mercury(II) chloride, $HgCl_2$. These three solutions are colorless and transparent; thus, they appear to be completely identical. If a stream of hydrogen sulfide gas ($H_2S$) is now passed through each of the solutions, in all three cases a similar appearing black precipitate will be formed. The precipitates are lead sulfide (PbS), silver sulfide ($Ag_2S$), and mercury(II) sulfide (HgS).

Thus, a chemist not knowing anything about the three solutions and carrying out just this test would not succeed in establishing the fact that the solutions contain three different metals. Moreover, the chemist would not be able to decide which of the solutions contained the silver, the lead, or the mercury, nor would he be able to exclude the possibility of all three metals being present in different combinations in all three solutions. When this situation arises, it is necessary to carry out additional tests on the products of the first reaction, or on reserved portions of the initial solutions. In other words, a metallic sulfide precipitate is not a product specific to a certain ion; rather, it is a product specific to a group of metallic ions.

Nevertheless, an experienced chemist will derive, even in cases such as this one, useful information from small particulars that would not be noticed by a person about to undertake qualitative analysis for the first time. Thus, the chemist will be able to distinguish the solution of mercury(II) chloride from the solutions of lead nitrate and silver nitrate because the precipitate formed by the reaction of $HgCl_2$ and $H_2S$ will first be whitish, then yellow, then brown, and finally black at the end of the reaction. The whitish, yellow, and brown colors are due to the formation of intermediate compounds prior to the formation of mercury(II) sulfide, compounds that contain chlorine in addition to mercury and sulfur.

In addition, it is important to observe carefully the appearance of precipitates as they form, noting their fineness, their tendency to settle, and their solubility on heating or on the addition of water. Both silver iodide and lead iodide, for example, are yellow and only very slightly

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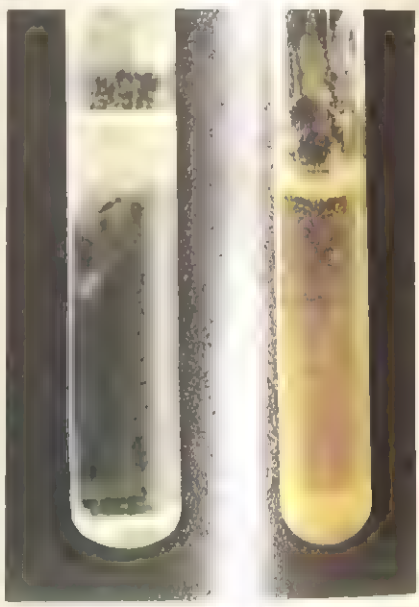
**KIPP'S GENERATOR**—This piece of equipment —once indispensable for qualitative analyses —was widely used for the production of hydrogen sulfide ($H_2S$) gas. This gas is used for precipitating many metals in the form of sulfides. Opening the stopper on the right permits the gas generating reaction to begin. Closing the stopper stops the reaction.

5

6a

6b



**LEAD IODIDE AND SI[illegible]ODIDE**—Consider two beakers containi[illegible]tions of silver nitrate and lead nitrate[illegible]ctively (illustration 6a). Suppose that thes[illegible]tions are acidified with a little nitric acid[illegible]d that a few cubic centimeters of a potass[illegible]iodide solution are then added. In both sol[illegible]s an instantaneous yellow precipitate forms. That is, a solid compound that tends to collect at the bottom of the beakers will be produced. Despite this similarity, however, the precipitates have very different characteristics. The silver iodide formed in the first beaker has a cheesy appearance; that is, it will appear to coagulate rather like sour milk.

The second precipitate, consisting of lead iodide, has a somewhat powdery appearance. This precipitate consists of tiny particles having the characteristic glitter of gold. Moreover, unlike the first precipitate, lead iodide can be dissolved in a large quantity of boiling water, giving rise to a colorless solution from which the tiny golden particles again precipitate on cooling (illustration 6b). It is impossible not to distinguish between these two iodides if these unmistakable characteristics are known.

Consequently, there should be no difficulty in identifying the two metals silver and lead. Analysis for silver and lead can, therefore, be discontinued at this point; no additional confirmatory tests are needed.

**THE LABORATORY E H**—The work bench in a chemical labor of very great importance. It must ha rge top in order to give the chemist c freedom of movement. The bench mu fitted also with gas jets for Bunsen burn well as with water faucets. Moreover, t ust be appropriate shelving for storing reagents. Of equal importance, distille must be readily available.

soluble in water. r can be precipitated from soluti wever, by means of the addition o lution containing iodide ions.

## THE SYSTEMA CHARACTER OF QUALITAT SOLUTION ANALYSIS

The reactions o rganic qualitative analysis are not c d out at random. Rather, they must f ow each other in a particular order. This is especially true when analyzing for metals; that is, for cations. Qualitative solution analysis is thus a systematic procedure.

The various metallic ions are subdivided into six analytic groups. Each of these groups of cations is precipitated by a specific reagent, provided that the reagent is used at the right time and in the correct order with respect to other reagents. The six groups are as follows:

The first group consists of all the cations whose chlorides are insoluble (the precipitating reagent is hydrochloric acid).

The second group consists of cations that precipitate as sulfides (the precipitating reagent is hydrogen sulfide gas bubbled through an unknown solution previously acidified with hydrochloric acid).

The third group consists of cations precipitated by ammonia (the precipitating reagent in ammonia—$NH_3$—in the presence of ammonium salts).

The fourth group consists of cations that precipitate as sulfides upon the addition of ammonium sulfide (the precipitating reagent is ammonium sulfide).

The fifth group consists of cations that precipitate as carbonates when ammonium carbonate is added to a previously ammoniated solution (the precipitating reagent is ammonium carbonate).

The sixth group consists of all the cations that do not have a common reagent.

## LABORATORY EQUIPMENT NEEDED BY CHEMISTS

Many reagents are required for a complete qualitative solution analysis. In addition to the group reagents listed above, reagents are needed for distinguishing the various metallic ions within each individual group; reagents needed for identifying anions; and the common acids and bases required for normal chemical operations. Many of these reagents must be available in both concentrated and dilute solutions. Concentrated acids are available commercially as follows: nitric acid, 63 percent; sulfuric acid, 96 percent; and hydrochloric acid, 37 percent. Dilute solutions, on the other hand, must be prepared in the proper concentrations required for specific analyses. In addition, various organic reagents have been added during recent years; many different organic compounds are available. At times, organic reagents can give extremely sensitive and very specific reactions. The laboratory glassware required for qualitative analysis, on the other hand, is rather modest. A few beakers, dropping bottles, glass rods, spatulas, and test tubes suitable for centrifuging are all that is required. Precipitation reactions are carried out in test tubes; the precipitates are then collected at the bottom by means of centrifuging. The solution remaining at the top of the tube will be clear.

Other equipment needed includes a centrifuge, preferably electric, a small controlled-temperature water bath, and several Bunsen burners.

8a

8b

8c

**LABORATORY EQUIPMENT**—Quite apart from the reagents needed for the precipitation of ions, the equipment of a laboratory used for qualitative analysis should include such items as centrifuges, water baths, and Bunsen burners. The centrifuge (electric centrifuges are in almost exclusive use today) has four elongated cavities in which four test tubes can be placed (illustration 8a). The centrifuge is used for separating precipitates from solutions. The water bath can be electric (illustration 8b), or a special test-tube holder (illustration 8c) can be placed in a container of water. Other equipment for qualitative analysis includes beakers, spatulas, glass rods, and dropping bottles.

# ABBREVIATIONS

| | |
|---|---|
| A | ampere |
| Å | Angstrom unit |
| abs | absolute |
| a-c | alternating current (as an adjective) |
| amu | atomic mass unit |
| atm | atmosphere |
| at. wt | atomic weight |
| AU | astronomical unit |
| avdp | avoirdupois |
| Bev | one billion electron volts |
| bhp | brake horsepower |
| bhp-hr | brake horsepower-hour |
| bp | boiling point |
| Btu | British thermal unit |
| C | temperature Celsius; temperature Centigrade |
| c | candle |
| cal | calorie |
| cfm | cubic feet per minute |
| cfs | cubic feet per second |
| cgs | centimeter-gram-second (system) |
| cl | centiliter |
| cm | centimeter |
| $cm^2$ | square centimeter |
| $cm^3$ | cubic centimeter |
| coef | coefficient |
| colog | cologarithm |
| cos | cosine |
| cot | cotangent |
| cp | candlepower |
| csc | cosecant |
| cu | cubic |
| cu ft | cubic foot |
| db | decibel |
| d-c | direct current (as an adjective) |
| doz | dozen |
| E | electromotive force |
| e | the base of the system of natural logarithms |
| ev | electron volt |
| F | temperature Fahrenheit |
| fp | freezing point |
| fpm | feet per minute |
| fps | feet per second |
| ft | foot; feet |
| $ft^2$ | square foot |
| $ft^3$ | cubic foot |
| ft-c | footcandle |
| ft-lb | foot-pound |
| G | universal gravitational constant |
| g | gram |
| gal | gallon |
| g-cal | gram-calorie |
| gpm | gallons per minute |
| gps | gallons per second |
| hr | hour |
| $h\nu$ | photon energy |
| hp | horsepower |
| Hz | hertz (cycles per second) |
| I | electric current |
| ID | inside diameter |
| in. | inch |
| $in.^2$ | square inch |
| $in.^3$ | cubic inch |
| in.-lb | inch-pound |
| ips | inches per second |
| j | joule |
| K | temperature Kelvin (absolute) |
| kcal | kilocalorie |
| kg | kilogram |
| kg-cal | kilogram-calorie |
| kg-m | kilogram-meter |
| $kg/m^3$ | kilograms per cubic meter |
| kgps | kilograms per second |
| km | kilometer |
| kv | kilovolt |
| kw | kilowatt |
| kwhr | kilowatt-hour |
| l | liter; lumen |
| lat | latitude |
| lb | pound |
| lb-ft | pound-foot |
| $lb/ft^2$ | pounds per square foot |
| $lb/ft^3$ | pounds per cubic foot |
| lb-in. | pound-inch |
| l-hr | lumen-hour |
| lin ft | linear foot |
| log | logarithm (common) |
| $\log_e$ | logarithm (natural) |
| long. | longitude |
| m | meter; minute (time, in astronomical circles) |
| $m^2$ | square meter |
| $m^3$ | cubic meter |
| ma | milliampere |
| Mev | one million electron volts |
| mg | milligram |
| mh | millihenry |
| mi | mile |
| $mi^2$ | square mile |
| min | minute |
| m-kg | meter-kilogram |
| ml | milliliter |
| mm | millimeter |
| $mm^2$ | square millim |
| $mm^3$ | cubic millime |
| $m\mu$ | millimicron |
| mph | miles per ho |
| mphps | miles per ho · second |
| mv | millivolt |
| $N$ | Avogadro's c nt |
| $n!$ | factorial $n$ |
| OD | outside dia |
| oz | ounce |
| pH | rating on ac kaline scale |
| ppm | parts per m |
| psi | pounds per s re inch |
| psia | pounds per s re inch absolute |
| R | temperature aumur; resistance |
| RA | right ascensi |
| rpm | revolutions p minute |
| rps | revolutions p second |
| sec | secant; sec |
| sin | sine |
| sp gr | specific gr |
| sq | square |
| tan | tangent |
| V | volt |
| VA | volt-amper |
| W | watt; work |
| yd | yard |
| $yd^2$ | square yard |
| $yd^3$ | cubic yard |

## SCIENTIFIC SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| $\alpha$ | alpha particle |
| $\beta$; $\beta^-$ | beta particle |
| $\beta^+$ | positron |
| $\gamma$ | gamma radiation |
| $\Delta$ | a small change; heat |
| $\lambda$ | wavelength; radioactive-decay constant |
| ma | milliampere |
| $\mu$c | microcurie |
| $\mu$f | microfarad |
| $\mu$in. | microinch |
| $\mu$m | micron |
| $\mu\mu$ | micromicron |
| $\mu\mu$f | micromicrofarad |
| $\nu$ | frequency; neutrino |
| $\pi$ | 3.14159; osmotic pressure |
| $\Sigma$ | the sum of |
| $\sigma$ | nuclear cross section (barns); area |
| $\Omega$ | electrical resistance (ohms) |
| $\omega$ | angular speed; angular velocity |
| $'$ | minute (angular measure) |
| $''$ | second (angular measure) |
| $\delta$ | male |
| ♀ | female |
| $>$ | is greater than |
| $<$ | is less than |
| $\propto$ | is proportional to |
| $\infty$ | infinity |
| $\sqrt{\ }$ | square root of |
| ° | degrees; temperature; angle measurement (example, 30°) |
| [ ] | molar concentration |
| + | positive electric charge; mixed with; plus |
| − | negative electric charge; single covalent bond; minus |
| = | equals; double covalent bond; produces |
| ≠ | does not equal |
| ≡ | triple covalent bond |
| → | produces; forms; chemical reaction |
| ⇄ | reversible chemical reaction |
| ↑ | gas produced by a chemical reaction |
| ↓ | precipitate produced by a chemical reaction |
| * | radioactive substance (follows symbol of element; example, Cl*) |

# THE ILLUSTRATED SCIENCE DICTIONARY

## Inductive Method to Lava

### KEY TO PRONUNCIATION

The diacritical marks are:

| | | |
|---|---|---|
| ə banan*a*, *a*but | e bet | th *th*in |
| ᵊ preceding l, m, n as in batt*le* | ē b*ea*t | t͟h *th*en |
| ȧ *e*lectric | i tip | ü r*u*le, f*oo*l |
| ər f*ur*ther | ī bite | u̇ p*u*ll, w*oo*d |
| a m*a*t | j *j*ob, ge*m* | ue German hübsch |
| ā d*ay* | ŋ si*ng* | u͞e French r*ue* |
| ä c*o*t, f*a*ther | ō b*o*ne | yü *u*nion |
| au̇ n*ow*, *ou*t | ȯ s*aw*, *a*ll | zh vi*s*ion |
| | ȯi c*oi*n | |

ˈ mark preceding the syllable with strongest stress.
ˌ mark preceding a syllable with secondary stress.

The system of indicating pronunciation in these volumes is used by permission from Webster's *Third New International Dictionary*, copyright 1961 by G. & C. Merriam Co., Publishers of the Merriam-Webster Dictionaries.

**inductive method** \in-'dək-tiv 'meth-əd\
The act of reasoning from a particular instance or particular instances to a general conclusion.

*The* INDUCTIVE METHOD *is used in making the generalization that "The sun always rises in the east."*

**inert** \in-'ərt\ *adj.*
CHEMISTRY. Describing a substance that does not usually react or combine with other substances to form compounds.

*Helium, argon and krypton are* INERT *gases.*

**inertia** \in-'ər-shə\ *n.*
PHYSICS. The characteristic of all matter that causes it to stay at rest, or stay in constant motion, unless an outside force acts upon it. It is a property independent of gravity and may be measured by any one of several units of mass.

*An object would have the same amount of* INERTIA *on the moon as on the earth, even though its weight would be less on the moon.*

Driver's body continues to move forward after car stops

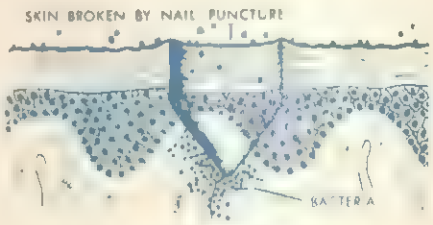
INERTIA

**inertial guidance** \in-'ər-shəl 'gī-dəns\
AERONAUTICS and ASTRONAUTICS. Control of a vehicle's course by self-contained accelerometers and gyroscopes that, in response to inertial forces, activate control mechanisms.

*The system of* INERTIAL GUIDANCE *that is used in some rockets and aircraft provides guidance without the use of any ground-located stations or components.*

**inertial system** \in-'ər-shəl 'sis-təm\
PHYSICS. A frame of reference within which Newton's laws of motion hold true; also, a set of points that do not move with respect to each other and that can be used to locate events or things.

*The earth, which appears to stand still, is an* INERTIAL SYSTEM *within which travel by automobile can be described.*



INFECTION

**infection** \in-'fek-shən\ *n.*
MEDICINE. Invasion of an animal or a plant by disease-producing organisms with consequent reactions of the tissues.

*Antiseptics are used on cuts and scratches to prevent* INFECTION.

INFERIOR

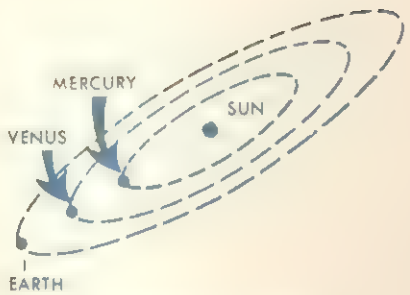
**inferior** \in-'fir-ē-ər\ *adj.*
1. ANATOMY. Describing the position of a structure or organ that is located below, or in a relatively lower position than,

some other part; also, sometimes, a structure that is directed or pointed downward. 2. Of poor quality.

*The* INFERIOR *vena cava is a large vein that returns blood from the lower parts of the body to the right side of the heart.*

**inferior planet** \in-'fir-ē-ər 'plan-ət\
ASTRONOMY. A planet, either Mercury or Venus, that orbits between the earth and the sun.

*Venus, an* INFERIOR PLANET, *is closer to the sun and therefore has a shorter period of revolution than does the earth.*



INFERIOR PLANET

**infinite** \'in-fə-nət\ *adj.*
MATHEMATICS. Having a larger value than any known quantity; continuing to infinity.

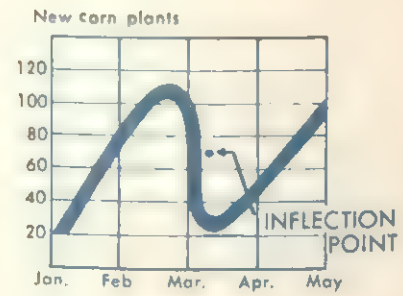
*The set of all positive integers is* INFINITE.

**infinite series** \'in-fə-nət 'si(ə)r-(,)ēz\
MATHEMATICS. The sum of a sequence of terms in which the sequence progresses according to some law, or plan, but never ends, regardless of how small the succeeding terms may become.

*An* INFINITE SERIES *may or may not approach a limit.*

**infinitesimal** \(,)in-,fin-ə-'tes-ə-məl\ *n.*
MATHEMATICS. A quantity, smaller than any known value, that approaches zero but never reaches it.

*Calculus is based on the concept of the* INFINITESIMAL.




**infinity** \in-'fin-ət-ē\ *n.*
MATHEMATICS. A concept whose value exceeds that of any finite value, or a dimensional space that is extended beyond finite bounds or limits.

*The cardinal number of the set of positive integers is* ℵ *(aleph-null), or countable* INFINITY.

**inflammable** \in-'flam-ə-bəl\ *adj.*
Used interchangeably with flammable. See *flammable.*

**inflection point** \in-'flek-shən 'point\
MATHEMATICS. A point on a curve at which the curve changes its direction of bending; also, more specifically, a point on the graph of a continuous function at which the graph changes its concavity.

*A curve of a continuous function has an* INFLECTION POINT *at*

*only those points where the values of the second derivative change signs.*

**inflorescence** \ˌin-flə-'res-ᵊn(t)s\ *n.*
BOTANY. A cluster of flowers, or the specific arrangement of flowers on a plant.

*A carrot plant has an umbrella-shaped* INFLORESCENCE.

**information retrieval** \ˌin-fər-'mā-shən ri-'trē-vəl\
ENGINEERING and MATHEMATICS. Any technique for recovering data or printed matter, often through the use of a computer complex or network.

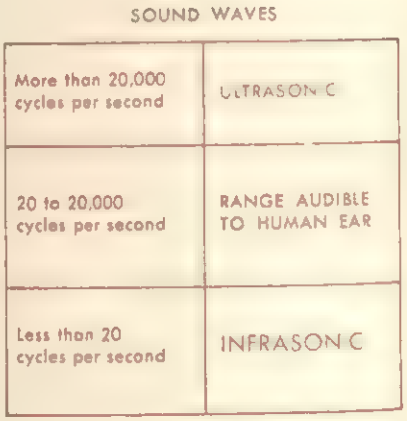
*A system of* INFORMATION RETRIEVAL *can provide quick access to book collections in many parts of the country.*

**infrared radiation** \ˌin-frə-'red ˌrād-ē-'ā-shən\
PHYSICS. The invisible rays of the electromagnetic spectrum that have a wavelength slightly longer than that of the visible color red, but shorter than that of radio waves. They may be sensed as heat radiation.

*Night photographs, without flashbulbs, may be made with film that is sensitive to* INFRARED RADIATION.

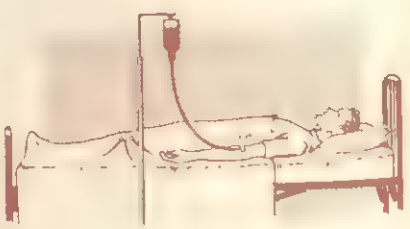
**infrasonic** \ˌin-frə-'sän-ik\ *adj.*
PHYSICS. Referring to sound waves that have a frequency below the range of human hearing.

INFRASONIC *waves may be tape-recorded and made audible by replaying the tape at a higher speed.*




**infusion** \in-'fyü-zhən\ *n.*
1. MEDICINE. The introduction of a liquid, such as a saline or glucose solution, into a vein. Infusion depends on gravity to cause the flow of liquid. 2. BIOLOGY. A suspension in water of decaying organic matter containing such microorganisms as protozoa. 3. CHEMISTRY. A water solution of soluble substances obtained by soaking a substance or tissue; also, the process of obtaining such a solution.

*A patient is often given an* INFUSION *of saline solution or blood plasma after an operation to keep his blood pressure up.*


INFUSION

**ingestion** \in-'jes(h)-chən\ *n.*
PHYSIOLOGY and ZOOLOGY. The act of taking in food or other substances; also, eating or swallowing.

*White corpuscles in infected tissues may take in bacteria by the process of* INGESTION *and use them as food.*

**inhalation** \ˌin-(h)ə-ˈlā-shən\ *n.*

PHYSIOLOGY. The process of breathing in or taking air into the lungs.

*In* INHALATION, *the slight lowering of pressure within the chest cavity results in air being pushed into the lungs by the higher outside pressure.*

**inherited characteristics** \in-ˈher-ət-əd ˌkar(-i)k-tə-ˈris-tiks\

BIOLOGY. Those physical traits, such as pattern baldness and eye color, that are transmitted from parent to offspring through genes.

*Blood types are* INHERITED CHARACTERISTICS, *but scars are acquired characteristics.*

**inhibition** \ˌin-(h)ə-ˈbish-ən\ *n.*

1. PHYSIOLOGY. The restraining or arresting of a body process. 2. CHEMISTRY. The slowing or stopping of a chemical reaction due to the presence of a given substance; negative catalysis.

INHIBITION *of the breathing rate may be effected by conscious effort.*

**inhibitor** \in-ˈhib-ət-ər\ *n.*

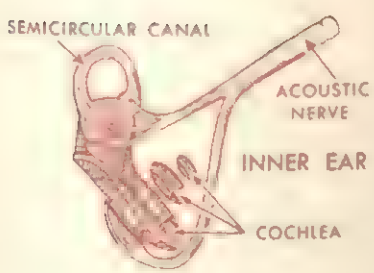
1. CHEMISTRY. A substance that, by its presence, slows down or stops a chemical reaction. 2. PHYSIOLOGY. Any substance that slows down or checks the function of a tissue or an organ. 3. MEDICINE. A chemical that holds in check the growth of microorganisms within the body.

*A rust* INHIBITOR *may be added to the fluid in the cooling system of an automobile.*

**inner ear** \ˈin-ər ˈi(ə)r\

ANATOMY and PHYSIOLOGY. The part of the ear that contains the bony labyrinth, the cochlea and the three semicircular canals, and that functions in both the sense of hearing and the sense of balance.

*The snail-shaped cochlea of the* INNER EAR *contains sensory nerve endings.*




**inoculation** \in-ˌäk-yə-ˈlā-shən\ *n.*

1. MEDICINE. The introduction of microorganisms, serums or other infective materials into an animal or a plant, causing a production of antibodies within the organism and resulting in immunity to the infection thus introduced. 2. BIOLOGY. The introduction of microorganisms into living tissue, either animal or plant, or into a culture medium.

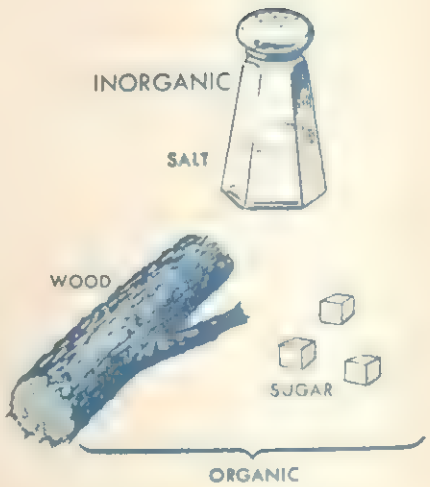
*The frequency of poliomyelitis is being reduced through* INOCULATION.

**inorganic** \ˌin-(ˌ)ȯr-'gan-ik\ *adj.*
CHEMISTRY. Referring to any substance not originally composed of living matter; also, frequently, referring to any substance that does not contain carbon compounds.

*Table salt is an* INORGANIC *substance, but wood and sugar are organic substances.*

**inorganic acid** \ˌin-(ˌ)ȯr-'gan-ik 'as-əd\
CHEMISTRY. Any acid that is not a compound of carbon; usually, a strong acid.

*Sulfuric acid is an* INORGANIC ACID.




**inphase** \'in-ˌfāz\ *adj.*
PHYSICS. Describing the condition of two or more series of repeating actions or events in which matching actions happen at the same time, such as the surges of electrical current in a given direction at exactly the same time in two separate electrical alternating current circuits.

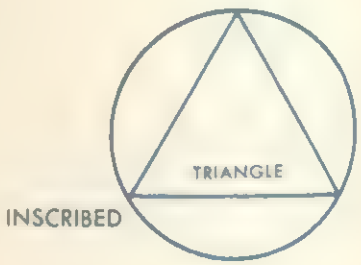
*The* INPHASE *component is the active part of an alternating current in a reactive circuit.*

**input** \'in-ˌpůt\ *n.*
PHYSICS. The signal or energy sent into a device, usually electrical or mechanical energy. Input is contrasted with output, which is the signal or energy produced by a device.

*The power* INPUT *of an electrical transformer is always greater than the output because some electrical energy is always converted into heat.*

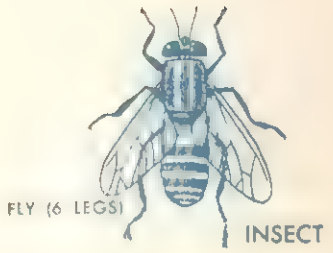
**inscribed** \in-'skrībd\ *adj.*
MATHEMATICS. Descriptive of a geometric figure placed inside, but not coincident with, an outer figure, so that the vertices of the inner figure (provided it is a polygon or polyhedron) lie on the outer figure or so that each side or face of the outer figure (provided it is a closed curve or curved surface) is tangent to the inner figure.

*A triangle* INSCRIBED *in a circle has its three vertices on the circle.*




**inscribed angle** \in-'skrībd 'aŋ-gəl\
MATHEMATICS. An angle whose vertex is on a circle and whose sides are chords of the circle.

*An* INSCRIBED ANGLE *may be part of an inscribed geometric figure.*




**insect** \'in-ˌsekt\ *n.*

ZOOLOGY. Any animal having three pairs of legs, three distinct body divisions and, usually, two pairs of wings.

*Because it has four pairs of legs, two body divisions and no wings, a spider is not an* INSECT.

**insectivorous** \ˌin-ˌsek-'tiv-(ə-)rəs\ *adj.*

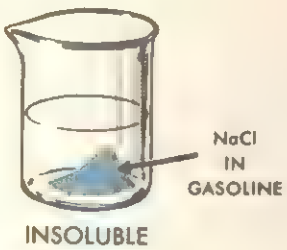
BIOLOGY. Describing animals whose food consists chiefly of insects, and plants that can obtain nitrogen from the bodies of trapped insects and other small animals.

*The woodpecker and the sundew plant are* INSECTIVOROUS *organisms.*

**insertion** \in-'sər-shən\ *n.*

ANATOMY. The end of a muscle that is attached to the bone that it moves.

*Fibrous tissue connects the* INSERTION *of a muscle to a bone.*




**insolation** \ˌin(t)-(ˌ)sō-'lā-shən\ *n.*

EARTH SCIENCE. The radiant energy received by the earth from the sun. The energy received depends upon the distance from the sun, the length of the day, the condition of the atmosphere and the angle of exposure.

INSOLATION *has a warming effect only if it is absorbed by the atmosphere or the earth.*

**insoluble** \(')in-'säl-yə-bəl\ *adj.*

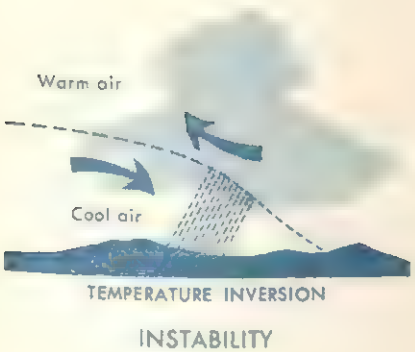
CHEMISTRY and PHYSICS. Describing something that does not dissolve.

*Table salt dissolves in water but is practically* INSOLUBLE *in alcohol.*

**inspiration** \ˌin(t)-spə-'rā-shən\ *n.*

PHYSIOLOGY and ZOOLOGY. Breathing in; inhalation.

*The muscles of the diaphragm contract during* INSPIRATION.




**instability** \ˌin(t)-stə-'bil-ət-ē\ *n.*

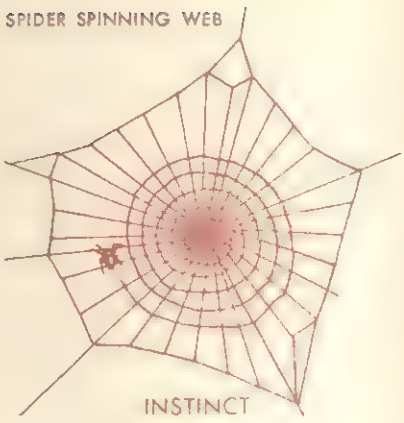
1. EARTH SCIENCE. A condition of the atmosphere in which there is an abnormal vertical distribution of temperature or moisture.
2. CHEMISTRY and PHYSICS. A condition that is not permanent; specifically, a temporary condition, as in a supersaturated solution or a supercooled liquid, in which crystals form rapidly when a small piece of solid is introduced; sometimes, the condition of being chemically unstable and therefore tending to react or decompose readily; see also *unstable* and *supercooled.*

INSTABILITY *of the atmosphere is a major cause of thunderstorms.*

**instinct** \'in-ˌstiŋ(k)t\ *n.*

PHYSIOLOGY and ZOOLOGY. A predictable behavior pattern characteristic of one species and largely determined by heredity.

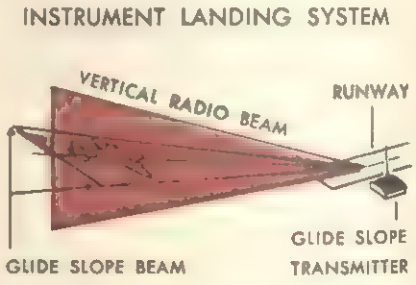
*The web-building* INSTINCT *of a spider is inherited.*




**instrument landing system** \'in(t)-strə-mənt 'land-iŋ 'sis-təm\

AERONAUTICS. A system of radio signals from the ground by which a pilot, with proper receiving instruments, can make an approach to a runway, even though he cannot see it; *abbr.* ILS.

*An* INSTRUMENT LANDING SYSTEM *differs from a ground-controlled approach system in that the latter involves continuous communication with a controller on the ground.*




**insulation** \ˌin(t)-sə-'lā-shən\ *n.*

CHEMISTRY and PHYSICS. A material used to prevent or reduce the passage of electricity, heat or sound from one area or substance to another.

*Air and porcelain are both used as electrical* INSULATION.

**insulin** \'in(t)-s(ə-)lən\ *n.*

PHYSIOLOGY and ZOOLOGY. A hormone that regulates carbohydrate metabolism in the bodies of some vertebrate animals.

*In man,* INSULIN *is produced by the islands of Langerhans in the pancreas.*

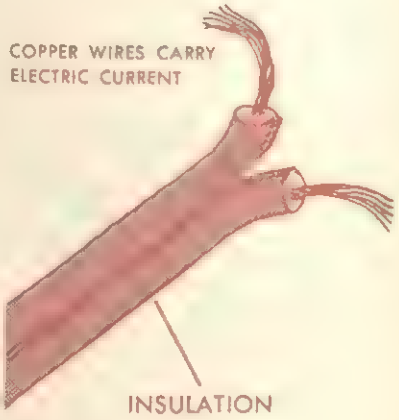
**integer** \'int-i-jər\ *n.*

MATHEMATICS. Any whole number, either positive or negative, or zero.

*When two integers are added, subtracted or multiplied, the result is always a unique* INTEGER.

**integral** \'int-i-grəl\

MATHEMATICS (Adj.). Relating to an integer or whole number, as distinguished from a fractional number; also, in algebra, referring to an expression or to an equation in which none of the variables appears in the denominator and all the exponents are positive; also, in calculus, relating to, or pertaining to, integration. (N.). The antiderivative, if one exists, of the function designated as the integrand; also, a function, usually termed the indefinite integral, whose derivative is the given function; also, the number, termed the definite integral, that is the difference between the values of the antiderivative at two specified points in the domain of the independent variable; also, geometrically, provided the integrand is a function whose independent variable is x, the number that represents the net



area of the portion of a Cartesian plane bounded by the graph of the integrand, the x-axis and the lines x = a and x = b, where a and b are the limits, or the bounds, of integration, the number referred to being originally defined in terms of the limit of a sequence of sums of areas of rectangles or of trapezoids so drawn as to approximate the desired number.

*In the* INTEGRAL $A = \int_1 x^2 dx$, $x^2$ *is the integrand and* $x = 1$ *and* $x = 2$ *are the limits of integration, and since the derivative of* $x^3/3 = x^2$, $A = 2^3/3 - 1^3/3 = 8/3 - 1/3 = 7/3$.

(ACTUAL SIZE)

INTEGRATED CIRCUIT

**integral calculus** \'int-i-grəl 'kal-kyə-ləs\

MATHEMATICS. The study of the process and the theory of integration and its application in solving varied physical problems, such as determining the lengths of arcs, the areas of surfaces, the volumes of solids, the centroids of plane areas and of solids, fluid pressures and work done by a variable force.

INTEGRAL CALCULUS *has many applications in engineering.*

**integrated circuit** \'int-ə-ˌgrāt-əd 'sər-kət\

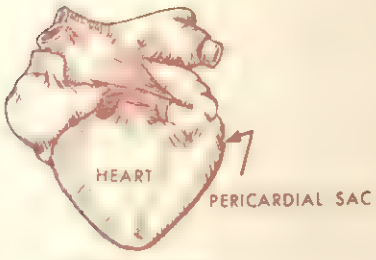
ENGINEERING and PHYSICS. A miniature electronic device consisting of a silicon chip into which the semiconductor equivalents of several hundred conventional electronic components have been formed and interconnected by various diffusion and etching procedures.

*The* INTEGRATED CIRCUIT *is particularly useful where weight and space are important, as in the electronic equipment carried by spacecraft.*

**integument** \in-'teg-yə-mənt\ *n.*

ANATOMY and BIOLOGY. The enclosing membrane or covering of the body of a plant or animal; also, the skin.

*The epidermis of a leaf is an* INTEGUMENT.




INTEGUMENT

**intensifier** \in-'ten(t)-sə-ˌfī(-ə)r\ *n.*

1. CHEMISTRY and PHYSICS. A substance that increases the magnitude, or amount, of a specific phenomenon; also, in photography, a chemical preparation that increases the contrast in a print or negative. 2. ENGINEERING. A device consisting basically of two connected cylinders of different diameters fitted with pistons and used to increase fluid force.

*Any one of several mercury compounds may be used as an* INTENSIFIER *to increase the blackness of an image on a photographic film or plate.*

**intensity** \in-'ten(t)-sət-ē\ *n.*

PHYSICS. An expression of the concentration of force, energy or

particles in a given area, volume or period of time; also, the amount of energy, such as light, electricity or sound, that passes through a given area in a certain time.

*The* INTENSITY *of light received by the eye from a given source decreases as the distance between the eye and the source increases.*

**intensity level** \in-'ten(t)-sət-ē 'lev-əl\
ENGINEERING. A comparison of the loudness of one sound with that of another, or with a preset standard level.

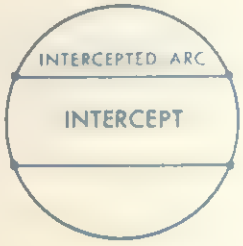
*Just before a telecast, the sound engineer checks the* INTENSITY LEVEL *of all microphone-amplifier systems.*

INTENSITY LEVEL
(of sound in decibels)

| | |
|---|---|
| AVERAGE HOUSE | 35 |
| AVERAGE OFFICE | 50 |
| TYPEWRITER | 72 |
| HEAVY TRAFFIC | 92 |
| PUNCH PRESS | 110 |
| PNEUMATIC DRILL | 130 |

**intercept** \,int-ər-'sept\ *v.*
MATHEMATICS. To bound or cut some portion of a surface, solid, line or plane.

*Two parallel lines* INTERCEPT *equal arcs on a circle.*

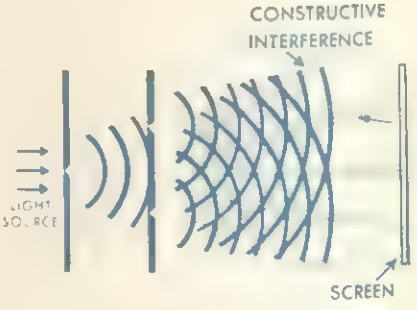



**interdependence** \,int-ər-di-'pen-dən(t)s\ *n.*
BIOLOGY. Mutual reliance of living organisms on one another for food, support, growth or development. For example, birds require plants for protection and food but, in turn, contribute to the survival of plants by eating harmful insects and transporting seeds.

INTERDEPENDENCE *among plants and animals is illustrated by the oxygen–carbon-dioxide cycle.*

**interference** \,int-ə(r)-'fir-ən(t)s\ *n.*
PHYSICS. The canceling or intensifying effect that results when two wave trains of the same, or nearly the same, frequency overlap each other. In the case of canceling (destructive interference), the crest of one wave overlaps the trough (depression) of the other wave.

*The production of a spectrum by a diffraction grating is due to* INTERFERENCE.



INTERFERENCE

**interferometer** \,int-ə(r)-fə-'räm-ət-ər\ *n.*
PHYSICS. An instrument used in the precise measurement of light wavelengths. It utilizes interference by splitting one light beam into two parts and bringing them back together after one travels a slightly-greater distance than the other.

*An* INTERFEROMETER *may be used to show that the speed of light is independent of the relative motion between the source and the receiver.*

INTERGALACTIC

**intergalactic** \ˌint-ər-gə-'lak-tik\ *adj.*

ASTRONOMY. Referring to space between and beyond the galaxies of the universe.

INTERGALACTIC *space can be considered to extend from the outer limits of interstellar space into the regions beyond.*

**interior angle** \in-'tir-ē-ər 'aŋ-gəl\

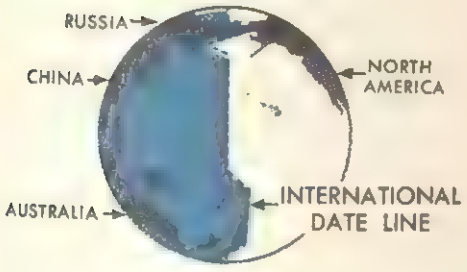
MATHEMATICS. An angle formed by two adjacent sides of a polygon; also, one of the four angles formed by two lines and the segment of a transversal cut off by them.

*The bisector of an* INTERIOR ANGLE *of a triangle divides the opposite side into segments proportional to the adjacent sides.*

**intermediate host** \ˌint-ər-'mēd-ē-ət 'hōst\

BIOLOGY and MEDICINE. A living animal or plant in which parasites in a larval or undeveloped state exist and from which the parasites pass for development in the final host.

*An* INTERMEDIATE HOST *may be unaffected by the parasitic larvae he carries.*




**international date line** \ˌint-ər-'nash-nəl 'dāt 'līn\

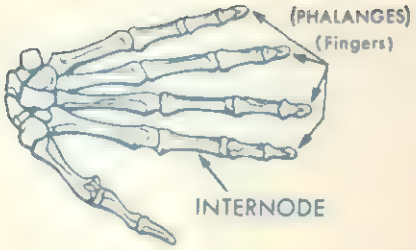
EARTH SCIENCE. A line, roughly along the 180-degree meridian, at which standard time changes forward or backward by 24 hours, or one calendar day.

*In crossing the* INTERNATIONAL DATE LINE *from east to west, the calendar date is moved ahead one day.*

**International Geophysical Year** \ˌint-ər-'nash-nəl ˌjē-ə-'fiz-i-kəl 'yi(ə)r\

EARTH SCIENCE. The period of about 18 months during 1957 and 1958 in which scientists from 67 nations pooled resources and techniques to learn more about the earth, atmosphere and space. Many research stations established during this period of time have continued to be used as international scientific observation centers; *abbr.* IGY.

*The launching of the first artificial satellite on October 4, 1957, was part of the planned program of the* INTERNATIONAL GEOPHYSICAL YEAR.




**internode** \'int-ər-ˌnōd\ *n.*

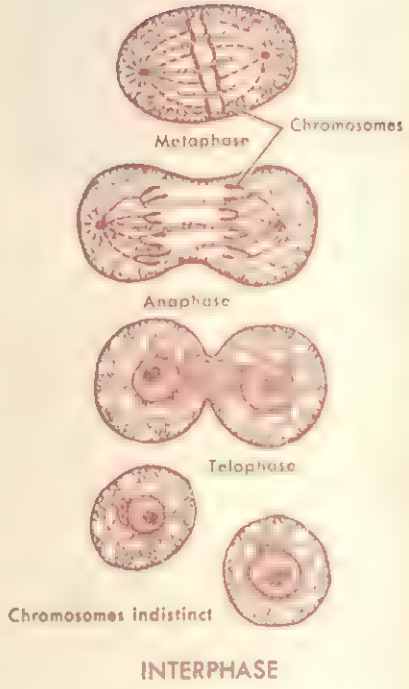
1. ANATOMY and ZOOLOGY. The part of a structure between two nodes; see *node* (1). 2. BOTANY. The section of a plant stem between two successive nodes; see *node* (2). 3. PHYSICS. The distance between two successive nodes in a standing wave system; see *node* (3).

*The part of a nerve fiber between two ganglia is an* INTERNODE.

**interphase** \'int-ər-ˌfāz\ *n.*

BIOLOGY. The stage of the nucleus of a cell between mitotic cell divisions. The stage is characterized by indistinction of chromosomes and is also called the resting stage.

*There is evidence that during* INTERPHASE *genes are duplicated.*



INTERPHASE

**interplanetary** \ˌint-ər-'plan-ə-ˌter-ē\ *adj.*

ASTRONAUTICS and ASTRONOMY. Describing the space between the planets in the solar system.

*Recent research indicates that there is probably some kind of sparse atmosphere throughout* INTERPLANETARY *space.*

**interpolation** \(ˌ)in-ˌter-pə-'lā-shən\ *n.*

MATHEMATICS. The process of finding or calculating intermediate values in a series other than by the assumed or given law of the series.

*The mantissa of a number having one more significant figure than those given in a table can be approximated by linear* INTERPOLATION.

**interpreter** \in-'tər-prət-ər\ *n.*

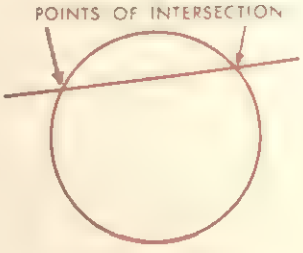
ENGINEERING and MATHEMATICS. A part of a computer that prints on a punch card the information punched on that card.

*One type of* INTERPRETER *prints data on a punch card at the same instant the card is punched.*

**interrogator-responder** \in-'ter-ə-ˌgāt-ər ri-'spän-dər\

ENGINEERING and PHYSICS. A type of transceiver that transmits a signal to a transponder and that receives and displays the reply from the transponder.

*Many commercial aircraft carry an* INTERROGATOR-RESPONDER *as an integral part of their distance-measuring equipment.*



INTERSECT

**intersect** \ˌint-ər-'sekt\ *v.*

MATHEMATICS. In geometry, to meet or cross at one or more common points; also, to have one or more points or elements in common.

*A circle and a straight line can* INTERSECT *at no more than two points.*

**interstellar** \ˌint-ər-'stel-ər\ *adj.*

ASTRONOMY. Referring to the space around the stars of the Milky Way or other galaxies; also, referring to the space beyond interplanetary space that extends to intergalactic space.

*Because* INTERSTELLAR *space is so vast, distances between stars are expressed in terms of light-years.*

INTRAVENOUS
(FEEDING)

**interval** \'int-ər-vəl\ *n.*

MATHEMATICS. The totality of points, or numbers, between two end points, either including the end points (closed interval) or excluding the end points (open interval).

*The closed* INTERVAL *that includes all real numbers from 1 through 10 may be designated symbolically as [1,10].*

**intestines** \in-'tes-tənz\ *n.*

ANATOMY. The alimentary canal, including the three parts of the small intestine (duodenum, jejunum and ileum) and the large intestine.

*In the* INTESTINES, *digestion is completed, absorption takes place and undigested materials are temporarily stored.*

**intravenous** \ˌin-trə-'vē-nēs\ *adj.*

ANATOMY and MEDICINE. Referring to the inside of a vein or to material that is put into the veins.

INTRAVENOUS *feedings of such nutrients as glucose and amino acids are sometimes necessary after certain operations.*

**intrusive** \in-'trü-siv\ *adj.*

EARTH SCIENCE. Describing igneous rock that solidified under the earth's crust rather than on its surface.

*Because it has cooled slowly,* INTRUSIVE *rock usually has large crystals.*

**inverse ratio** \(')in-'vərs 'rā-(ˌ)shō\

MATHEMATICS. The reciprocal ratio, or the ratio between the reciprocals of quantities or numbers.

*The* INVERSE RATIO *for the ratio 3:5 is the ratio 5:3.*

$$F = \frac{m_1 \times m_2}{d^2}$$

WHEN F = FORCE IN DYNES
$m_1$ = UNIT OF POLE STRENGTH
$m_2$ = UNIT OF POLE STRENGTH
d = DISTANCE BETWEEN POLES, IN CENTIMETERS

INVERSE-SQUARE LAW
(for magnetic forces)

**inverse-square law** \(')in-'vərs 'skwa(ə)r 'lȯ\

PHYSICS. A principle stating that intensity of energy received from a point source decreases as the square of the distance between the receiver and the source. Thus, when the distance is doubled, the intensity is ¼ of the original intensity, and when the distance is tripled, the intensity is ⅑ of the original intensity.

*The* INVERSE-SQUARE LAW *holds true for gravitational and magnetic forces, as well as for many types of energy.*

**inverse variation** \(')in-'vərs ˌver-ē-'a-shən\

MATHEMATICS. A relation between two quantities in which one

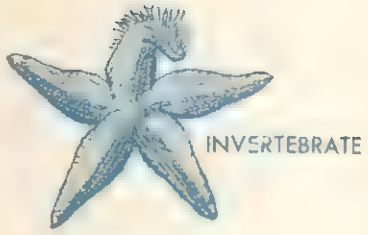
quantity increases and the other decreases, or vice versa, in such a manner that their product remains constant.

*The equation $lw = 24$ expresses an* INVERSE VARIATION *because the product of $l$ and $w$ is always the same number.*

**inversion** \in-'vər-zhən\ *n.*

1. EARTH SCIENCE. A condition of the atmosphere in which the temperature increases with height instead of the usual decrease with height; also, folding of rock strata back over themselves, resulting in a reversal of the order of succession. 2. CHEMISTRY and PHYSICS. A process of changing a substance that rotates plane-polarized light clockwise to one that rotates the same light in the opposite direction. 3. MATHEMATICS. In proportions, an interchange of the first and second terms and of the third and fourth terms; also, the process of finding an inverse.

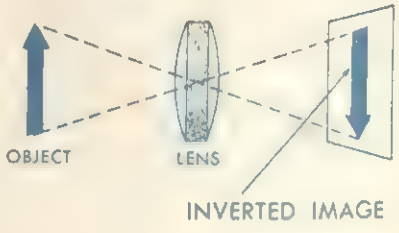
*An* INVERSION *near the earth's surface is a common cause of ground fog.*




**invertebrate** \(')in-'vərt-ə-brət\ *n.*

ZOOLOGY. Any animal that does not have an internal backbone, such as protozoa, shellfish and insects.

*An* INVERTEBRATE *is a member of the subkingdom that includes about 95 percent of all animals.*




**inverted image** \in-'vərt-əd 'im-ij\

PHYSICS. An image that is upside down relative to the object it represents.

*Human eyes project an* INVERTED IMAGE *on the retina, but the brain learns to interpret the image as being right side up.*

**inverter** \in-'vərt-ər\ *n.*

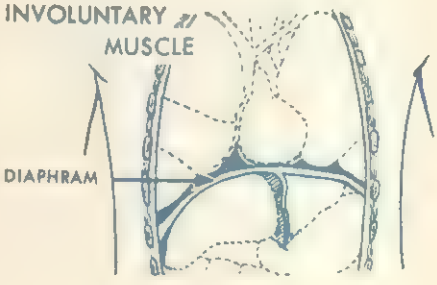
ENGINEERING. A device that changes direct current into alternating current.

*One type of* INVERTER *is a gas-filled vacuum tube.*

**invisible light** \(')in-'viz-ə-bəl 'līt\

PHYSICS. Electromagnetic radiation that has wavelengths shorter or longer than those of visible light; ultraviolet and infrared radiations.

*Most* INVISIBLE LIGHT *can be detected and recorded by special photographic film.*

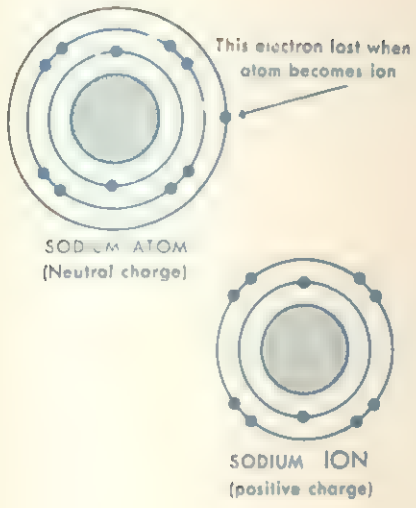



**involuntary muscles** \(')in-'väl-ən-ˌter-ē 'məs-əlz\

ANATOMY. Muscles that are stimulated to action by the lower centers of the nervous system or by hormone action and are

therefore not consciously controlled, as muscles of the heart; see *voluntary muscles.*

*The muscles of the diaphragm may act either as voluntary or* INVOLUNTARY MUSCLES.




**iodine** \'ī-ə-ˌdīn\ *n.*

CHEMISTRY. A blue-gray crystalline element with nonmetallic chemical properties. Iodine is a member of the halogen family of elements that includes chlorine and bromine. Symbol, I; atomic number, 53; atomic weight, 126.9044.

IODINE *is most common as a dilute solution in ethyl alcohol and is called tincture of iodine.*

**ion** \'ī-ən\ *n.*

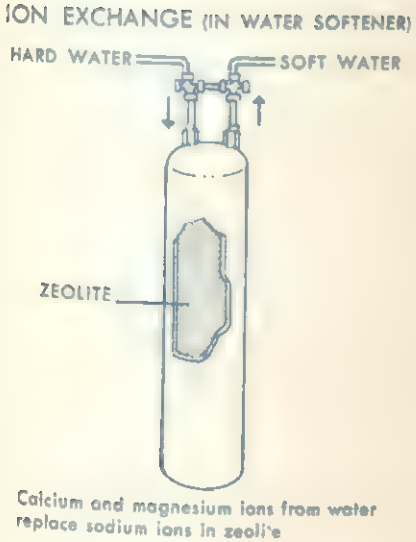
CHEMISTRY and PHYSICS. An atom, or group of atoms, that has gained or lost one or more electrons and is therefore electrically charged plus or minus.

*In a crystal of table salt, there is one positive* ION *(sodium) for every negative ion (chloride).*

**ion engine** \'ī-ən 'en-jən\

ASTRONAUTICS and ENGINEERING. A rocket engine in which a heavy element, such as mercury or cesium, is ionized by chemical or nuclear heat. The ions are accelerated electrically to provide thrust.

*Because an* ION ENGINE *produces very low thrust, it will be most useful in interplanetary space, where the gravitational force of the planets is small.*




**ion exchange** \'ī-ən iks-'chānj\

CHEMISTRY and ENGINEERING. A process by which certain ions in solution are removed, and different ions of the same charge take their place. Ion exchange is frequently accomplished by flowing a solution over a solid with which ions will be traded. Under special conditions, the direction of trading may be reversed. The process does not result in a noticeable structural change in the solid but may give the solution different properties.

ION EXCHANGE *is used to soften water.*

**ionic bonds** \ī-'än-ik 'bändz\

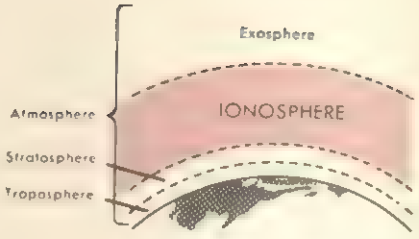
CHEMISTRY. The attracting forces between ions of opposite charge in a crystalline compound.

*A crystal of table salt is composed of sodium and chloride ions held rigidly in place by* IONIC BONDS.

**ionic theory** \ī-'än-ik 'thē-ə-rē\
CHEMISTRY. A theory of ion production. See *ionization.*

**ionization** \ˌī-ə-nə-'zā-shən\ *n.*
CHEMISTRY and PHYSICS. The process by which ions are produced from molecules or atoms. It may involve breaking molecules apart so that the fragments each have unequal numbers of plus and minus electrical charges. It may also involve heating, or otherwise energizing, atoms to the extent that one or more electrons leave, thereby producing positive ions.

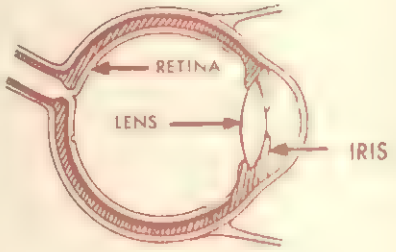
*The passage of an alpha particle through the air causes* IONIZATION *of oxygen and nitrogen molecules along the path of the particle.*



IONOSPHERE

**ionosphere** \ī-'än-ə-ˌsfi(ə)r\ *n.*
EARTH SCIENCE. A region of the earth's atmosphere beginning about 50 miles above the surface and extending to about 650 miles. It consists of scattered air particles that are ionized by solar radiation.

*The* IONOSPHERE *contains several layers that reflect certain radio waves back to the earth.*

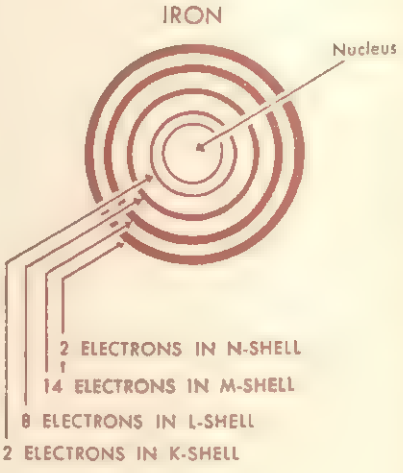



**ion propulsion** \'ī-ən prə-'pəl-shən\
ASTRONAUTICS and ENGINEERING. Rocket propulsion by an ion engine. See *ion engine.*

**IR**
An abbreviation for interrogator-responder. See *interrogator-responder.*

**iridescence** \ˌir-ə-'des-ᵊn(t)s\ *n.*
A display of rainbowlike colors as a result of the diffraction of light reflected from corrugated or closely-ribbed surfaces, or by interference in a thin film, such as a soap bubble.

IRIDESCENCE *is a characteristic of quartz crystals and mother-of-pearl.*



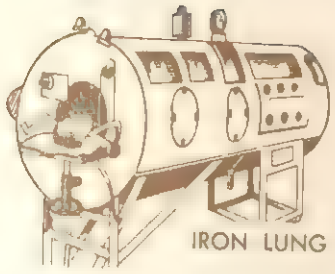

**iris** \'ī-rəs\ *n.*
ANATOMY. The pigmented, or colored, structure at the front of the eye, located directly in front of the lens and surrounding the pupil, or opening, through which light passes to the retina.

*Involuntary muscles change the size of the* IRIS *to control the amount of light reaching the retina.*

**iron** \'ī(-ə)rn\ *n.*
CHEMISTRY. A metallic element that is malleable, ductile and

magnetic. It is seldom found chemically pure. Symbol, Fe; atomic number, 26; atomic weight, 55.85.

*Carbon is used in most industrial processes for obtaining* IRON *from its ores.*




**iron lung** \'ī(-ə)rn 'ləŋ\

MEDICINE. A large metal respirator that encloses the entire body, with the exception of the head, and maintains breathing artificially by first increasing and then decreasing the air pressure around the body.

*An* IRON LUNG *is used in cases in which the nerves that control the muscles used in breathing have been damaged or destroyed.*

**irradiation** \(,)ir-,ād-ē-'ā-shən\ *n.*

The process of exposing matter to some kind of radiation, such as ultraviolet light or X ray.

*Microorganisms in food and clothing may be destroyed by* IRRADIATION.

ISLAND

**irrational numbers** \(')ir-'(r)ash-nəl 'nəm-bərz\

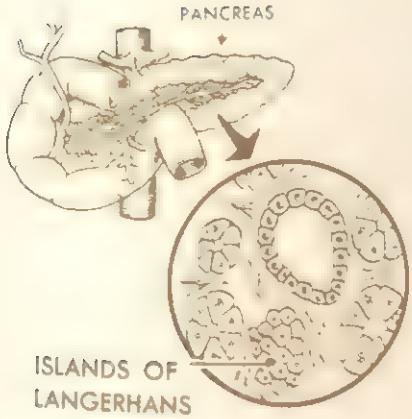
MATHEMATICS. Numbers that cannot be expressed as the quotient of two numbers.

*The numbers represented by the symbols* $\sqrt{2}$ *and* $\sqrt{3}$ *are* IRRATIONAL NUMBERS.

**irritability** \,ir-ət-ə-'bil-ət-ē\ *n.*

BIOLOGY and PHYSIOLOGY. The ability of living cells, tissues or organisms to react or respond to both internal and external stimuli. This ability is one of the distinguishing characteristics of all living things.

*The responses of organisms to light, heat, sound and touch are examples of* IRRITABILITY.




**island** \'ī-lənd\ *n.*

EARTH SCIENCE. A land area smaller than a continent and completely surrounded by water.

*The* ISLAND *of Hawaii is made up of five volcanoes that rise nearly six miles from the ocean bottom.*

**islands of Langerhans** \ī'-ləndz əv 'läŋ-ər-,hän(t)s\

ANATOMY and PHYSIOLOGY. Small groups of glandular cells within the pancreas that function as ductless or endocrine glands and that produce the hormone insulin; also known as the islets of Langerhans.

*Insulin, the secretion from the* ISLANDS OF LANGERHANS, *goes directly into the bloodstream and not into the digestive tract.*

**isobars** \'ī-sə-ˌbärz\ *n.*

EARTH SCIENCE. Lines drawn on weather maps through points having the same barometric pressure.

*By studying the arrangement of* ISOBARS *on a weather map, a meteorologist can predict the direction and speed of a storm.*

**isoelectric point** \ˌī-(ˌ)sō-i-'lek-trik 'pȯint\

CHEMISTRY. That relative acidity, or *p*H value, for a colloidal solution of a specific protein in water at which the protein particles are not attracted to either a positive or a negative electrode. It occurs when there is no electrical charge difference between the protein particles and the water and is a property useful in identifying unknown proteins.

*A given colloidal solution of protein has its lowest electrical conductivity and its lowest viscosity at its* ISOELECTRIC POINT.

**isogonal** \ī-'säg-ən-ᵊl\ *adj.*

MATHEMATICS. Having equal angles.

*An equilateral triangle is an* ISOGONAL *triangle.*

**isogonic lines** \ˌī-sə-'gän-ik 'līnz\

EARTH SCIENCE. The lines drawn on a map connecting points that have equal magnetic declination. Along any one of these lines, a compass would point to magnetic north at a constant angle east or west of true north.

*Because the earth's magnetic poles move slightly over a period of time, new maps showing* ISOGONIC LINES *must be made periodically.*

ISOGONIC LINES

**isomers** \'ī-sə-mərz\ *n.*

1. CHEMISTRY. Two or more molecular compounds composed of the same number and kind of atoms but in which the molecules have different arrangements of atoms. Properties such as the boiling point, density and rate of chemical reaction may be different in isomers. 2. PHYSICS. Two or more radioactive nuclei having the same atomic number and atomic mass but existing for a measurable time in different energy states. The form of higher energy decays to the lower energy form (isomeric transition).

*Ordinary ether and butyl alcohol are* ISOMERS *having the formula* $C_4H_{10}O$.

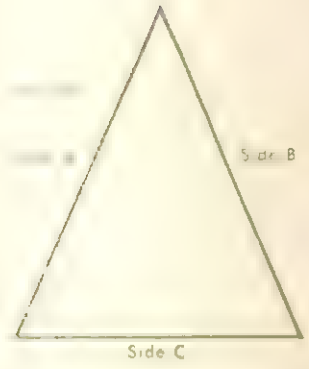
**isomorph** \'ī-sə-ˌmȯrf\ *n.*

BIOLOGY. An organism similar to another organism of different species or race, resulting from convergence.

*The resemblance of an* ISOMORPH *to another organism is superficial, rather than morphological.*

**isoperimetric** \ˌī-sō-ˌper-ə-'me-trik\ *adj.*
MATHEMATICS. Descriptive of two or more closed geometric figures that have equal perimeters.

ISOPERIMETRIC *figures generally do not have equal areas.*



SOSCELES TRIANGLE

**isosceles trapezoid** \ī-'säs-ə-ˌlēz 'trap-ə-ˌzȯid\
MATHEMATICS. A four-sided figure having two parallel sides and two nonparallel sides and whose nonparallel sides are equal.

*Base angles of an* ISOSCELES TRAPEZOID *are equal to each other.*

**isosceles triangle** \ī-'säs-ə-ˌlēz 'trī-ˌaŋ-gəl\
MATHEMATICS. A triangle having two equal sides.

*If one base angle of an* ISOSCELES TRIANGLE *is known, its other angles can be determined.*

**isostasy** \ī-'säs-tə-sē\ *n.*
EARTH SCIENCE. The state of balance between high and low masses of the earth's crust. The higher masses have a lower average density, thus projecting above the heavier parts of the crust.

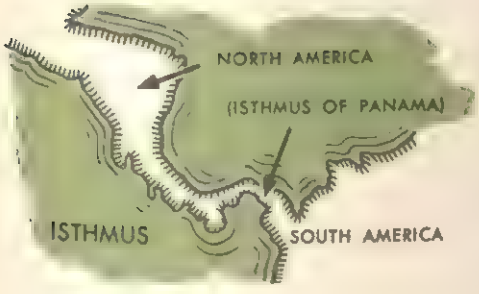
*An assumption made in explaining mountain structures by* ISOSTASY *is that mountains have deep roots of the same material as the mountains themselves.*

**isotherm** \'ī-sə-ˌthərm\ *n.*
EARTH SCIENCE. A line drawn on a weather map connecting points having the same temperature at, or during, a given time.

*An* ISOTHERM *representing average temperature of a large area generally has an east-west orientation.*

**isotope** \'ī-sə-ˌtōp\ *n.*
CHEMISTRY. An atom that differs from another atom, or other atoms, of the same element because it has a different number of neutrons in its nucleus (different atomic weight).

*Deuterium is an* ISOTOPE *of hydrogen.*



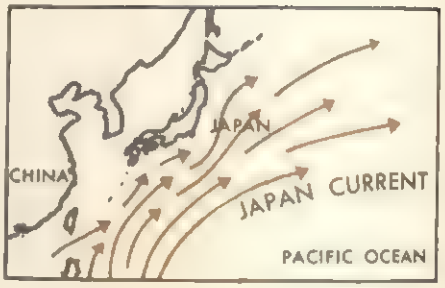

**isthmus** \'is-məs\ *n.*
EARTH SCIENCE. A narrow strip of land that connects two large areas of land, or a large area of land and a peninsula.

*North and South America are joined by the* ISTHMUS *of Panama.*

# J

**Japan current** \jə-'pan 'kər-ənt\
EARTH SCIENCE. A warm current, originating in tropical waters, that flows past Japan and northeastward across the Pacific Ocean.

*The* JAPAN CURRENT *has a warming effect on the Pacific Coast of North America.*




**JATO** \'jāt-(,)ō\ *adj.*
AERONAUTICS. Referring to a jet-assisted takeoff. It is a means of reducing the takeoff distance of piston-engined aircraft by using small rocket engines to increase takeoff speed.

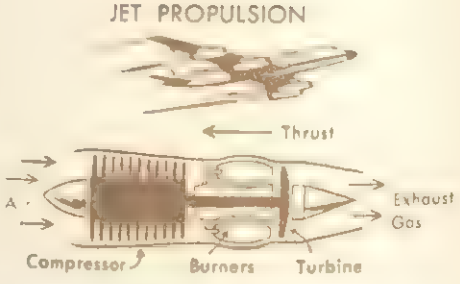
JATO *rockets are most frequently used by military aircraft and are attached to either the fuselage or the wings.*

**jejunum** \jə-'jü-nəm\ *n.*
ANATOMY. One of three parts of the small intestine. It lies between and connects the other two, the duodenum and the ileum.

*The* JEJUNUM *is approximately 9.5 feet in length.*

**jet propulsion** \'jet prə-'pəl-shən\
AERONAUTICS and ASTRONAUTICS. The thrust produced when pressurized gases or liquids escape through an exhaust nozzle; the forward thrust of an aircraft or sea craft by one or more jets of burning gases.

JET PROPULSION *can be demonstrated by releasing an inflated toy balloon and observing its resulting forward motion.*




**jet stream** \'jet 'strēm\
EARTH SCIENCE. A high-speed current of wind that occurs at altitudes of 20,000 to 40,000 feet and moves from west to east.

*By flying in a* JET STREAM, *a pilot flying eastward may increase his ground speed by 50 to 100 miles per hour.*

**joint** \'jȯint\ *n.*
1. ANATOMY and ZOOLOGY. A place where two or more bones are connected or joined; also, a junction between bones or between cartilage and bone. 2. BOTANY. The node of a stem or grass where leaves or branches are developed. 3. EARTH SCIENCE.

A fracture, or break, formed along a plane of weakness in a rock mass.

*The ball-and-socket* JOINT *in the hip permits free movement in several directions.*

$$H = \frac{I^2Rt}{4.18} = 0.239I^2Rt$$

WHEN H = HEAT IN CALORIES

I = CURRENT IN AMPERES

R = RESISTANCE IN OHMS

t = TIME IN SECONDS

JOULE'S LAW

**joule** \'jü(ə)l\ *n.*

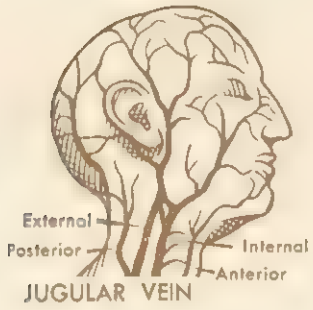
PHYSICS. A unit of energy or work equal to 10,000,000 ergs. It is a derived unit of the meter-kilogram-second system of units and equals the energy expended when an unbalanced force of one newton acts through a distance of one meter.

*When an electrical appliance uses electrical energy at the rate of one* JOULE *per second, it is rated at one watt.*

**Joule's law** \'jü(ə)lz 'lȯ\

PHYSICS. A principle stating that the heat produced in a conductor by an electric current is proportional to the resistance of the conductor, the square of the current and the time the current flows.

*According to* JOULE'S LAW, *heat produced by the electricity flowing through a 100-watt light bulb for one hour will heat one kilogram of water from approximately 57° F. to its boiling point.*




JUGULAR VEIN

**jugular vein** \'jəg-yə-lər 'vān\

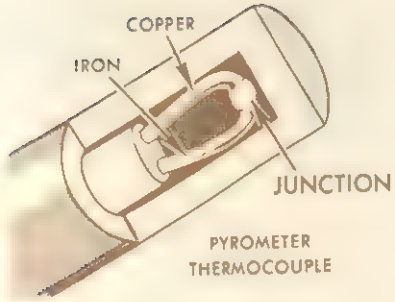
ANATOMY. Any one of four major veins in the neck that returns blood from the head back to the heart.

*An external* JUGULAR VEIN *receives blood from the face and neck.*

**Julian calendar** \'jül-yən 'kal-ən-dər\

ASTRONOMY. A calendar instituted by Julius Caesar in Rome in 46 B.C. in which the year was divided into 365 days with one day added to the month of February every fourth (or leap) year. After modification by Pope Gregory XIII in 1582, it became the basis for our present-day calendar.

*The* JULIAN CALENDAR *was modified because its year did not correspond closely enough with the actual period of the earth's revolution around the sun.*




**junction** \'jəŋ(k)-shən\ *n.*

PHYSICS. A surface or point at which two different objects or materials come in contact with each other or are joined together; see *p-n junction* and *transistor*.

*A* JUNCTION *of iron wire and brass wire, often called a thermocouple, will produce an electrical voltage when heated.*

# K

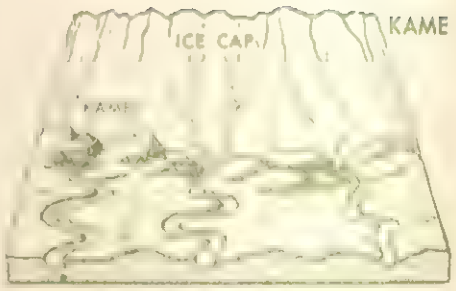
**°K.**

An abbreviation for a temperature measured on the Kelvin temperature scale. See *Kelvin temperature scale.*

**kame** \'kām\ *n.*

EARTH SCIENCE. A cone-shaped mound made of layers of gravel and sand formed by the sediment carried to the edge of a glacier by streams of meltwater.

*The layered sand and gravel in a* KAME *is called stratified drift.*




**karst topography** \'kärst tə-'päg-rə-fē\

EARTH SCIENCE. A land area with an irregular surface of sinkholes, caused when surface water and ground water dissolve the soluble bedrock, usually limestone.

*In an area having* KARST TOPOGRAPHY, *there are few surface streams because most of the drainage is underground.*

**Kelvin temperature scale** \'kel-vən 'tem-pər-ˌchü(ə)r 'skāl\

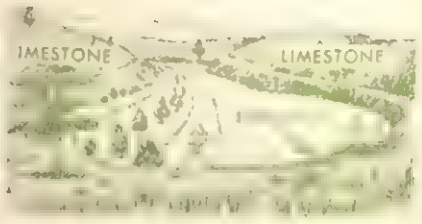
CHEMISTRY and PHYSICS. A temperature scale that starts with zero as the lowest temperature possible (about −273.1° C.) and has no negative numbers; also called absolute temperature scale; *abbr.* K.

*On the* KELVIN TEMPERATURE SCALE, *the boiling point for water is about 373° K.*

**Kennelly-Heaviside layer** \'ken-ᵊl-ē-'hev-ē-ˌsīd 'lā-ər\

EARTH SCIENCE. A layer in the ionosphere 50 to 80 miles above the earth's surface containing ionized air particles that make long-distance shortwave radio communications possible by reflecting and refracting certain frequencies; also called E layer; see *ionosphere.*

*The height of the* KENNELLY-HEAVISIDE LAYER *varies from day to night, accounting in part for accompanying differences in radio reception.*



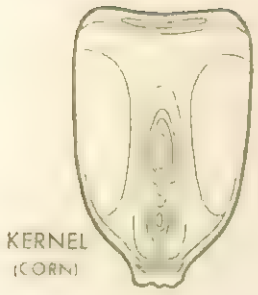

KARST TOPOGRAPHY

**Kepler's laws** \'kep-lərz 'lȯz\

ASTRONOMY. Three laws concerned with the motion of planets, first stated by Johannes Kepler: (*a*) The orbit of a planet is an ellipse with the sun at one focus. (*b*) A line joining the planet with the sun sweeps out equal areas of space in equal time

intervals. (*c*) The squares of the periods of any two planets are proportional to the cubes of their average distances from the sun.

KEPLER'S LAWS *also apply to the motion of the moon and artificial satellites around the earth, except that "the earth" replaces "the sun" in the statement of the laws.*


KERNEL (CORN)

**kernel** \'kərn-ᵊl\ *n.*

1. BOTANY. A plant seed, protected by a covering or husk, that has the ability to grow when planted or when it falls in a place favorable for growth; also, the inner portion of a seed. 2. ANATOMY. A hard swelling beneath the skin; also, a small gland or structure resembling a gland.

*Near the top of a corn* KERNEL, *on the same side as the embryo, is found a tiny point, the silk scar, where the corn silk was attached.*

**kerosine**\'ker-ə-ˌsēn\ *n.*

CHEMISTRY. A colorless mixture of hydrocarbons, obtained by the fractional distillation of petroleum and used as a fuel. It was once called coal oil because it was originally obtained by the destructive distillation of coal; also spelled kerosene.

KEROSINE *is used as fuel in many turbine and turbojet engines.*

KETTLE

**ketones** \'kē-ˌtōnz\ *n.*

CHEMISTRY. A class of compounds characterized by two hydrocarbon radicals joined by a carbonyl (CO) group.

*Acetone, the most common of the* KETONES, *will dissolve many substances that are insoluble in water.*

**kettle** \'ket-ᵊl\ *n.*

EARTH SCIENCE. A basinlike depression formed when a detached block of glacial ice that has been partially or completely covered with drift melts.

*A lake or swamp may form if water drains into a* KETTLE.

KEY

**key** \'kē\ *n.*

1. EARTH SCIENCE. A low island of sand or coral located near a coast. A key is often one of a chain of islands. 2. BIOLOGY and EARTH SCIENCE. A chart, table or outline that contains a short description of the identifying characteristics of a group of plants, animals, rocks or fossils and that is used to identify unknown specimens.

*Key West is located on a* KEY *at the southern tip of Florida.*

**key punch** \'kē 'pənch\

ENGINEERING. A keyboard-operated machine that cuts coded holes in punch cards, which are then read by computers or accounting machines; also called card punch.

*When one key of a* KEY PUNCH *is depressed, the card advances one space through the machine.*

**kidney** \'kid-nē\ *n.*

ANATOMY. In man, one of a pair of bean-shaped glandular organs located at the back of the abdominal cavity, one on each side of the spinal column. The kidney functions as a filter to remove waste products of metabolism from the blood.

*A* KIDNEY *in adults usually weighs four to six ounces.*

**kilocalorie** \'kil-ə-,kal-(ə-)rē\ *n.*

PHYSICS. The amount of heat that is necessary to raise the temperature of a kilogram of water one degree C. It is equal to 1,000 calories, or 4,184 joules.

*The calorie used to express the energy content of food is really a* KILOCALORIE.

**kilocycle** \'kil-ə-,sī-kəl\ *n.*

PHYSICS. A unit equal to 1,000 cycles that is commonly used to mean 1,000 cycles per second in expressing the frequency of radio and sound waves; *abbr.* kc or kc/s.

*A* KILOCYCLE *is equal to 1/1,000 megacycle.*

**kilogram** \'kil-ə-,gram\ *n.*

MATHEMATICS. A unit in the metric system equal to 1,000 grams, or 2.2046 pounds, and used to measure mass and weight.

*The* KILOGRAM *is a standard unit of mass in most scientific work.*

KILOCYCLE

**kilometer** \ kil-'äm-ət-ər\ *n.*

MATHEMATICS. A unit in the metric system equal to 1,000 meters, 3,280 feet or 0.6214 mile, used to measure distance.

*Km is the abbreviation for* KILOMETER.

**kilowatt** \'kil-ə-,wät\ *n.*

PHYSICS. A unit of power equal to 1,000 watts, or to energy consumption at the rate of 1,000 joules per second. It usually is used in reference to electrical power.

*An electric motor rated at one horsepower uses electrical energy at a rate of about ¾* KILOWATT.

**kilowatt-hour** \'kil-ə-ˌwät-'au̇(-ə)r\ *n.*
PHYSICS. A unit of energy or work equal to the amount of energy used by an electrical device operating for one hour and having a power rating of one kilowatt.

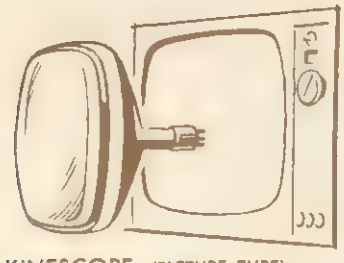
*In the future, nuclear reactors may produce electricity at a lower cost per* KILOWATT-HOUR *than conventional coal and steam plants do now.*

**kindling temperature** \'kin-(d)liŋ 'tem-pər-ˌchu̇(ə)r\
CHEMISTRY. The lowest temperature at which a substance will start to burn.

*Paper has a lower* KINDLING TEMPERATURE *than does coal.*

**kinescope** \'kin-ə-ˌskōp\ *n.*
ENGINEERING. The picture tube of a television receiver. In operation, a beam of electrons is moved across and up and down over the fluorescent screen while, at the same time, the intensity of the beam is varied in accordance with light and dark areas of the image produced in the transmitting camera.

*In the* KINESCOPE, *the beam of electrons is directed by a variable magnetic field.*


KINESCOPE (PICTURE TUBE)

**kinesiology** \kə-ˌnē-sē-'äl-ə-jē\ *n.*
MEDICINE and PHYSIOLOGY. The study of the muscular movements of the body and of how the body's organs are affected by these motions.

*The principles of* KINESIOLOGY *are used in the rehabilitation of infantile paralysis patients.*

**kinesthetic sense** \ˌkin-əs-'thet-ik 'sen(t)s\
PHYSIOLOGY. The perception of balance, body position, weight and muscular movement. Kinesthetic sensations arise from nerve endings in various parts of the body, as in muscles and joints.

KINESTHETIC SENSE *enables a person to know the relative positions of his arms and legs even in a dark room.*

KINETIC ENERGY

**kinetic energy** \kə-'net-ik 'en-ər-jē\
PHYSICS. The energy of motion; the ability of an object to do work because of its motion.

*At impact, much of a bullet's* KINETIC ENERGY *is changed to heat.*

**kinetics** \kə-'net-iks\ *n.*

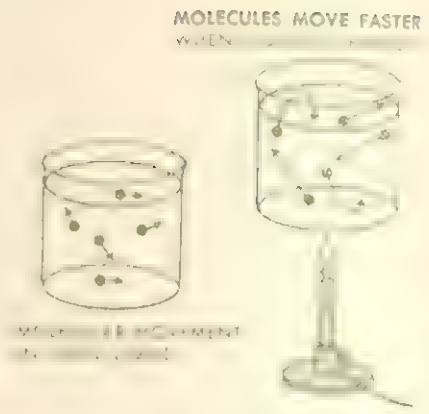
1. PHYSICS. The study of the effects of force on the motion of objects. 2. CHEMISTRY. The study of the speeds at which chemical reactions occur.

*The techniques for putting satellites in orbit are based on* KINETICS.

**kinetic theory** \kə-'net-ik 'thē-ə-rē\

PHYSICS. A theory that explains diffusion, heat expansion and variations in gas pressures on the basis of moving molecules, atoms or ions. The theory assumes that all molecules, except those at absolute zero, are in motion.

*According to the* KINETIC THEORY, *raising the temperature of a substance is the same as causing its molecules to move faster.*




KINETIC THEORY

**kingdom** \'kiŋ-dəm\ *n.*

BIOLOGY. One of the two large groups, plant or animal, into which all living things are classed.

*Organisms that belong to the animal* KINGDOM *usually have flexible cell walls.*

**klystron** \'klī-ˌsträn\ *n.*

PHYSICS. A special type of electron tube that replaces the usual vacuum tube in electronic circuits where the frequencies are 500 megacycles or higher.

*The invention of the* KLYSTRON *was necessary before radar could become practical.*

**km**

An abbreviation for kilometer. See *kilometer.*

**knee jerk** \'nē 'jərk\

PHYSIOLOGY. The natural reflexive movement of the leg caused by tapping the tendon below the kneecap while the leg is bent; also called patellar reflex.

*The* KNEE JERK *test is sometimes made to detect injury to the spinal cord.*

**knot** \'nät\ *n.*

MATHEMATICS. A unit of speed equal to one nautical mile, or

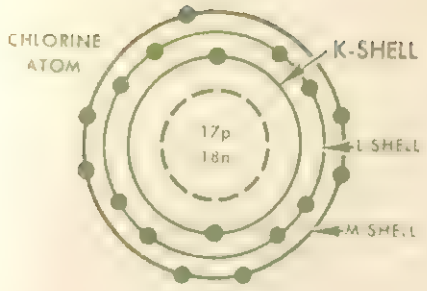
6,080 feet, per hour and used in expressing the speed of aircraft, ships, ocean currents and winds.

*It is not technically correct to say a ship travels 20 knots per hour, since the unit* KNOT *already includes the time factor.*

**Koch's postulates** \'kȯks 'päs-chə-ˌlāts\

BIOLOGY and MEDICINE. The four requirements for proving that a particular microorganism has caused a particular infectious disease. They are, in sequence, (1) the particular microorganism must be identified wherever the disease is found; (2) the same microorganism must be grown in isolation in a culture outside the host; (3) the same microorganism must, when transferred from the culture to a host, cause the original disease; (4) the same microorganism must be identified in the diseased host.

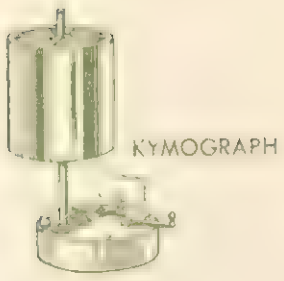
KOCH'S POSTULATES *were developed by the German doctor Robert Koch, who applied them to identify the microbes causing anthrax, tuberculosis and cholera.*




**Krebs cycle** \'krebz 'sī-kəl\

BIOLOGY. A sequence of oxidation-reduction reactions that forms a central phase of cell metabolism. The cycle involves citric acid and many enzymes and coenzymes and generates an energy supply for the cell in the form of adenosine triphosphate; also called citric acid cycle.

*Waste materials formed during the* KREBS CYCLE *are given off by the cell as water and carbon dioxide.*




**K-shell** \'kā-ˌshel\ *n.*

CHEMISTRY and PHYSICS. One of the seven principal energy levels, identified by the letters K, L, M, N, O, P and Q, that electrons may occupy in an atom; the first, or lowest, principal energy level that electrons may occupy in the Bohr model for the atom.

*Some artificial radioisotopes capture, or absorb, an electron from the* K-SHELL *in the process of radioactive decay.*

**kymograph** \'kī-mə-ˌgraf\ *n.*

MEDICINE and PHYSIOLOGY. A device that consists of a rotating drum covered by a cylinder of paper on which a record of wave or pulselike movements may be traced.

*A* KYMOGRAPH *is powered by an electric motor or by a steel spring.*

# L

**laboratory** \'lab-(ə-)rə-ˌtōr-ē\ *n.*

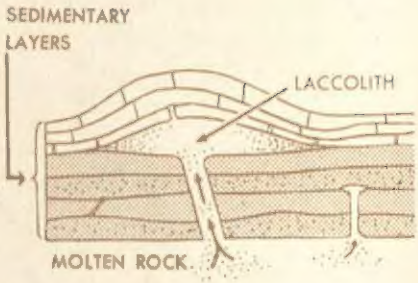
A place specially equipped for scientific research, experimentation or testing; also, an environment, such as a woods, the ocean floor or outer space, that is used in scientific research.

*An industry may have a* LABORATORY *for testing current products and for developing new products.*

**laccolith** \'lak-ə-ˌlith\ *n.*

EARTH SCIENCE. A dome-shaped mass of igneous rock, often granite, lying between layers of sedimentary rock. It is formed from molten rock that has been forced between the sedimentary layers.

*A* LACCOLITH *forces the overlying sedimentary rocks into a domed structure.*




LACCOLITH

**lachrymal glands** \'lak-rə-məl 'glandz\

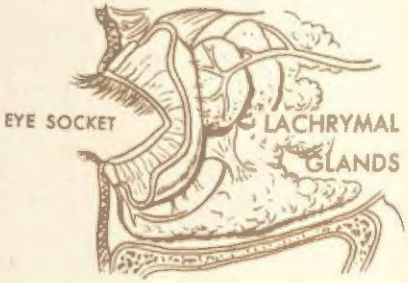
ANATOMY. The tear glands that lie at the upper and outer part of the eyeball and open by several ducts inside the upper eyelids at the outer corners of the eyes.

*Tears from the* LACHRYMAL GLANDS *contain a material that inhibits bacterial growth.*

**lacquer** \ 'lak-ər\ *n.*

CHEMISTRY. A protective or decorative coating that is composed of certain carbon compounds dissolved in a volatile, or quickly-evaporating, solvent.

*Paint dries by reacting with oxygen, but* LACQUER *dries by the evaporation of solvent.*




**lacteal** \'lak-tē-əl\

1. ANATOMY (N.). A lymph vessel that takes up the chyle from the small intestine and passes it on to the blood. 2. ZOOLOGY (Adj.). Pertaining to milk; also, carrying or containing the milky fluid chyle, a product of fat digestion.

*A* LACTEAL *is an important part of the lymphatic system.*

**lactose** \'lak-ˌtōs\ *n.*

CHEMISTRY. $C_{12}H_{22}O_{11}$. A sugar that occurs in milk; a disaccharide.

*Milk sours as enzymes turn* LACTOSE *into lactic acid.*

LAGOON

**lagoon** \lə-'gün\ *n.*

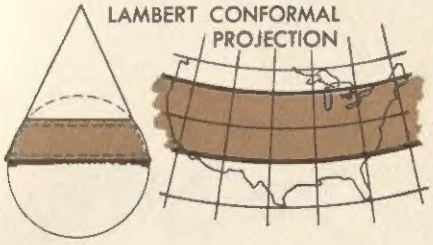
EARTH SCIENCE. A body of salt water between the mainland and a low barrier island or within an atoll; also, a body of fresh water that connects with a larger lake or a river.

*A* LAGOON *may be a shallow saltwater lake with restricted connections to the ocean.*

**lake** \'lāk\ *n.*

1. EARTH SCIENCE. A body of water surrounded by land. 2. CHEMISTRY. A colored, insoluble substance permanently fixed within the fiber of yarn or cloth as a result of certain dyeing processes.

*A* LAKE *that has an outlet through which dissolved materials flow usually remains a freshwater lake.*




**Lambert conformal projection** \'lam-bərt kən-'fȯr-məl prə-'jek-shən\

EARTH SCIENCE. A map of the earth's surface, made by projecting surface features onto a cone that intersects the earth at two standard parallels. The resulting map has less than two-percent distortion of the area between the standard parallels.

*The aeronautical charts of the United States are based on a* LAMBERT CONFORMAL PROJECTION *with standard parallels of 33 and 45 degrees north.*

**lampblack** \'lamp-ˌblak\ *n.*

CHEMISTRY. The element carbon in the form of very fine particles; also, the soot produced by burning oil in a limited supply of air.

LAMPBLACK *is used as a coloring substance in the production of ink, paint and automobile tires.*

| | |
|---|---|
| Lanthanum La 57 | Terbium Tb 65 |
| Cerium Ce 58 | Dysprosium Dy 66 |
| Praseodymium Pr 59 | Holmium Ho 67 |
| Neodymium Nd 60 | Erbium Er 68 |
| Promethium Pm 61 | Thulium Tm 69 |
| Samarium Sm 62 | Ytterbium Yb 70 |
| Europium Eu 63 | Lutetium Lu 71 |
| Gadolinium Gd 64 | |

LANTHANIDE SERIES

**land breeze** \'land 'brēz\

EARTH SCIENCE. The movement of air from land areas toward a lake or sea. Such a movement usually occurs at night and in the early morning when land temperatures are lower than water temperatures.

*A* LAND BREEZE *results when air cooled by radiation produces a high-pressure area over land and a low-pressure area over water.*

**lanthanide series** \'lan(t)-thə-ˌnīd 'si(ə)r-(ˌ)ēz\

CHEMISTRY. Fifteen elements (including lanthanum) that are similar to lanthanum in physical and chemical properties, with

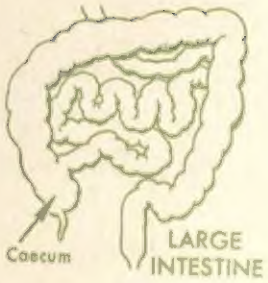
atomic numbers from 57 through 71; also called rare-earth elements.

*Several minerals containing elements of the* LANTHANIDE SERIES *are found along the seacoast in the Carolinas.*

**lapse rate** \'laps 'rāt\

EARTH SCIENCE. The rate at which temperature decreases as altitude increases; temperature gradient.

*The normal* LAPSE RATE *is a 3.5° F. decrease in temperature per 1,000-foot increase in altitude.*




**large intestine** \'lärj in-'tes-tən\

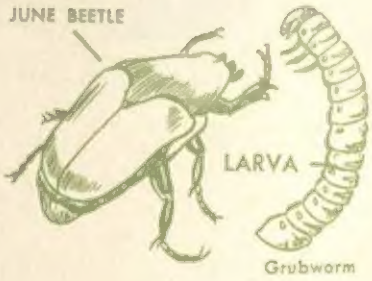
ANATOMY. That part of the digestive tract that consists of the cecum, the colon and the rectum.

*A large part of the water present in the material entering the* LARGE INTESTINE *is reabsorbed into the bloodstream.*

**larva** \'lär-və\ *n.*

ZOOLOGY. An early stage in the development of those animals that show a marked change in structure when they become adult.

*The young insect that hatches from an egg is known as a* LARVA *until it develops into a pupa.*




**larynx** \'lar-iŋ(k)s\ *n.*

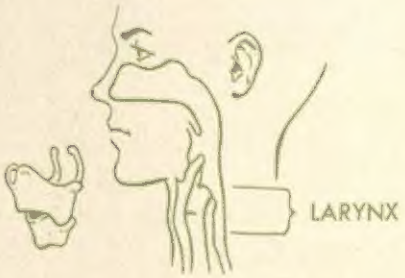
1. ANATOMY. The organ of voice, that is situated between the trachea and the base of the tongue. The larynx contains the vocal cords that, by contracting and relaxing, produce changes in the pitch of the voice. 2. ZOOLOGY. A similar structure in other animals.

*The sound of the voice comes from the* LARYNX, *but it is modified by the nasal chambers and the mouth.*

**laser** \'lā-zər\ *n.*

PHYSICS. An electronic device for generating light that has a narrow frequency range and is confined to a small, nondiverging beam. It produces photons that are in phase with each other.

*The word* LASER *is made from the initial letters of the phrase "light amplification by stimulated emission of radiation."*




**latent** \'lāt-ᵊnt\ *adj.*

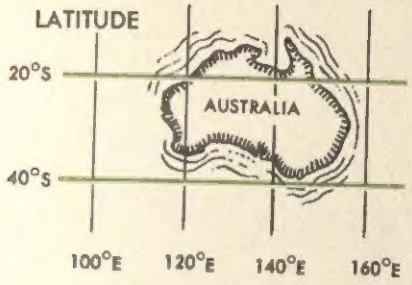
Pertaining to something present but inactive; dormant.

LATENT *viruses may live in an organism for a long time without producing disease.*

**latent heat** \'lāt-ᵊnt 'hēt\

PHYSICS. The heat absorbed or released when a substance changes state, as from solid to liquid or liquid to gas, as opposed to the heat required to change the temperature of the substance.

*The approximate 540 calories of heat required to change 1 gram of liquid water at 100° C. to steam at 100° C. is an example of* LATENT HEAT.




**latent image** \'lāt-ᵊnt 'im-ij\

PHYSICS. An invisible image formed on a light-sensitive emulsion by exposure to light. The image can be made visible through the developing processes used in photography.

*The rate at which a* LATENT IMAGE *is formed is not affected by temperature.*

**lateral** \'lat-ə-rəl\ *adj.*

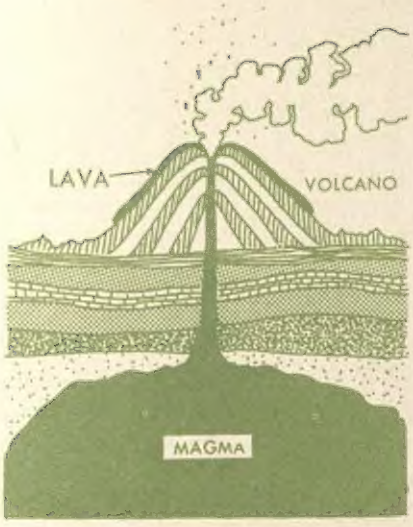
Pertaining to the side; also, situated on the side; also, branching from the middle toward the side.

*A* LATERAL *moraine is one that is deposited along the side of a glacier.*

**latex** \'lā-teks\ *n.*

1. BOTANY. A milky secretion produced by, or found in, certain plants. 2. CHEMISTRY. A suspension of colloidal particles of rubber in a liquid.

LATEX *collected from the sapodilla tree is used in the manufacture of chewing gum.*




**latitude** \'lat-ə-ˌt(y)üd\ *n.*

EARTH SCIENCE. The measurement in degrees of distance north or south of the equator, the angle being between the equatorial plane and a line from the center of the earth to the earth's surface.

*One degree of* LATITUDE *is equal to a distance of approximately 69 miles anywhere on the earth's surface.*

**lava** \'lä-və\ *n.*

EARTH SCIENCE. Molten rock that escapes from the earth's interior through breaks in the earth's surface; also, the rock formed when the molten material has solidified.

*Molten rock is called magma when inside the earth and* LAVA *when it flows onto the earth's surface.*